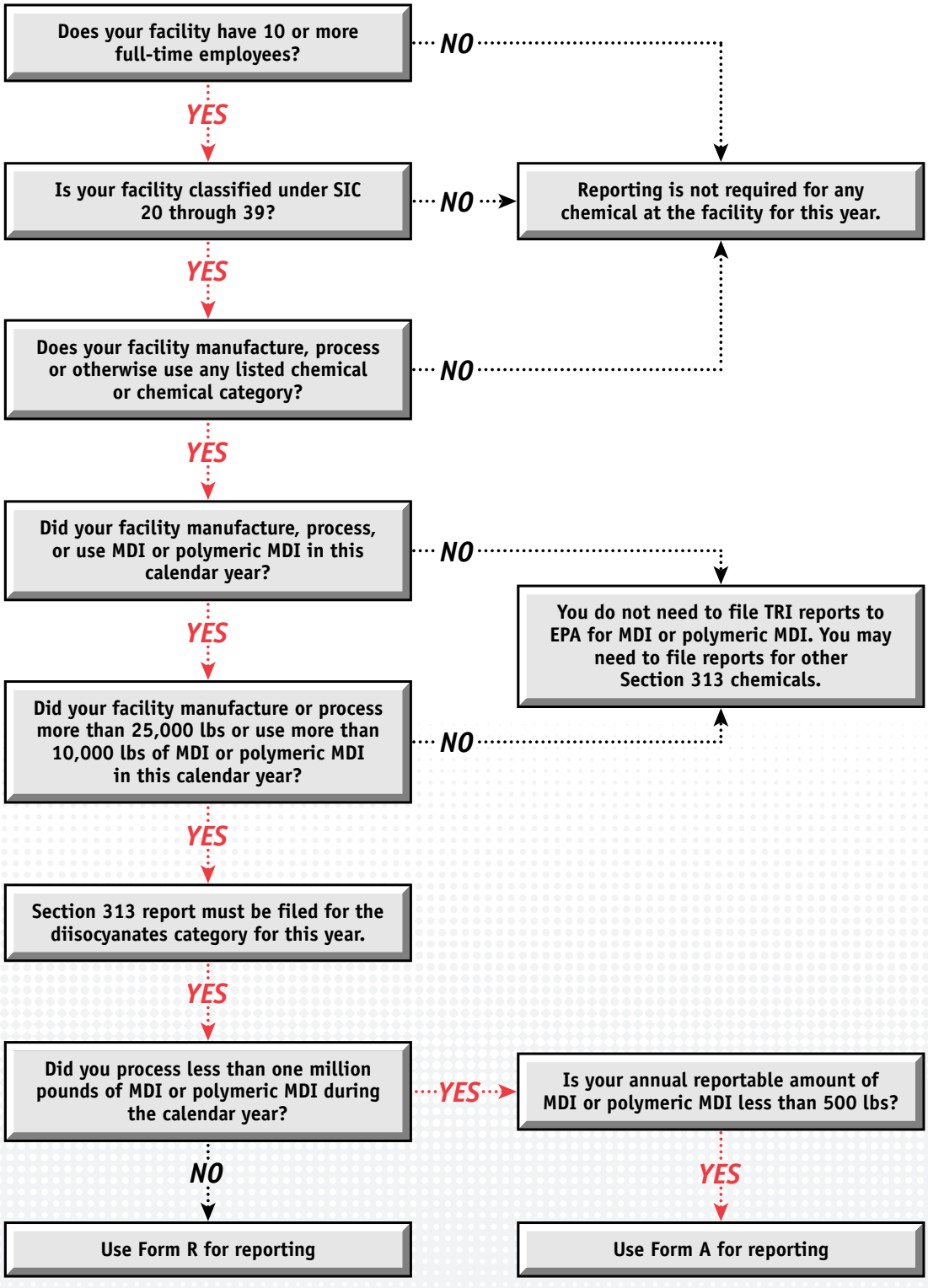
ALLIANCE FOR THE POLYURETHANES INDUSTRY

A BUSINESS UNIT OF THE AMERICAN PLASTICS COUNCIL

MDI/Polymeric MDI Emissions Reporting Guidelines For the Polyurethane Industry



For Section 313 of EPCRA and State Reporting

Note to Readers:

This document reviews the requirements and offers guidance for reporting releases of certain listed chemicals of interest to members of the polyurethane industry under the provisions of Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA). Its principal purposes are to:

- Assist companies in the polyurethane industry in completing the Environmental Protection Agency's (EPA) Form A or Form R,
- Outline suggested techniques for estimating emissions for certain chemicals in the "diisocyanates" category listing under EPCRA, specifically 4,4'-methylene diphenyl diisocyanate (MDI) and mixtures of MDI and polymeric MDI (PMDI), and
- Provide examples of calculating MDI/polymeric MDI emissions associated with storage tank losses, fugitive releases, and stack emissions based on applied applications.

The methodologies used to estimate releases of 4,4'-methylene diphenyl diisocyanate (MDI) and mixtures of MDI and polymeric MDI (PMDI) have been developed using standard techniques, but may not be suitable for estimating releases of other chemicals. The information provided in this document is offered in good faith and believed to be reliable, but is made WITHOUT WARRANTY, EXPRESS OR IMPLIED, AS TO MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, OR ANY OTHER MATTER. This document is not intended to provide emissions data for any particular product or process. Scenarios that have been selected are believed to be representative of situations where releases may occur. Other scenarios not reflected in this document may involve releases as well. It is the responsibility of all manufacturers, processors or users of any listed chemical to know and understand the reporting obligations, and to provide accurate information, in accordance with the provisions of the law. Consult your own legal and technical advisors for specific advice applicable to your own facility.

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Introduction and Background

The purpose of this document is to provide manufacturers, processors and other users of certain chemicals in the polyurethane industry with guidance on fulfilling their obligation to report releases of listed chemicals in accordance with the provisions of Section 313 of the Emergency Planning and Community Right-to- Know Act (EPCRA). In particular, this document outlines approaches for estimating emissions from the processing and use of 4,4'-methylene diphenyl diisocyanate (MDI) and mixtures of MDI and polymeric MDI (PMDI) in the absence of specific data on emissions. MDI and PMDI are EPCRA-listed chemicals in the "diisocyanates" category listing (N-120) for which reports must be filed.

Section 313 requires affected facilities to provide information on (1) routine and accidental releases of specific listed chemicals and mixtures of chemicals into the environment, (2) transfers to off-site facilities, and (3) waste treatment methods, and the efficiency of those methods. It also requires reporting on the name, location and type of business; the identity of the listed chemical(s) or chemical mixture(s) involved, and whether the chemical is manufactured, processed or otherwise used at the facility; and an estimate of the maximum amount of the chemical present at the facility at any time during the year. EPCRA-required information must be reported on the Annual Section 313 Toxic Chemical Release Form R. In certain circumstances, however, facilities may be able to report using the 313 Toxic Chemical Release Form A, which requires significantly less information.

Facilities are also required to comply with the provisions of the Pollution Prevention Act of 1990 (PPA). The PPA requires that source reduction and detailed information about on-site waste treatment and recycling be reported. Definitions of "source reduction," "treatment," "recycling" and the like should be reviewed and your activities reported accordingly.

Reported information is placed in the Environmental Protection Agency's (EPA) Toxic Release Inventory (TRI) database, where it is made publicly available via the Internet and through the annual publication of the Toxic Release Inventory.

Use of TRI Database

When Congress passed the Emergency Planning and Community Right-to-Know Act (EPCRA) in 1986, they were mandated to promote contingency planning for chemical releases and provide the public with previously unavailable information about toxic and hazardous chemicals in their communities.

Under Section 313(h) of EPCRA, Congress clearly provides for the wide distribution of the industry information gathered. The release forms required under this section are intended to provide information to federal, state and local governments and the public. This includes citizens of communities surrounding the covered facilities. These forms provide information about chemical releases to the environment that will enable government agencies, researches, and other individual conducting research and data gathering to develop appropriate regulations, guidelines, and standards**.** Since the TRI data has become available, it has become a useful resource for many different organizations:

- Federal, state and local governments use TRI data to set the priorities and allocate environmental protection resources.
- Regulators use TRI data to set permit limits, measure compliance with those limits, and target facilities for enforcement activities.
- Governments use TRI data to assess or modify taxes and fees based on toxic emissions or overall environmental performance.
- Communities use TRI data to begin dialogues with local facilities and to encourage them to reduce their emissions, develop pollution prevention plans, and improve safety measures.
- Industry uses TRI data to identify pollution prevention opportunities, set goals for toxic chemical release reductions, and demonstrate its commitment to and progress in reducing emissions.
- Public interest groups use TRI data to identify the potential need for new environmental regulations or

improved implementation and enforcement of existing regulations.

- Consultants and others use TRI data to identify business opportunities, such as marketing pollution prevention and control technologies to TRI reporting facilities.

Therefore, it is important that reports be as accurate as possible. Overestimating emissions can lead regulators and others to seek imposition of controls that are not scientifically justified, while underestimating emissions can risk enforcement action by the Agency.

Historical Perspective on TRI Reporting for Diisocyanate Users

MDI was part of the original list of toxic chemicals subject to EPCRA 313. In 1994, however, EPA created a "diisocyanates" category, containing 18 specific isocyanates. Beginning in Reporting Year 1995, a covered facility that exceeded a threshold for the diisocyanate category had to file a TRI report.

Specifically, instead of submitting separate reports for MDI, PMDI and other isocyanates, reports must be aggregated for all isocyanates used and released by a facility. For example, if a facility processes 10,000 pounds of pure MDI and 15,000 pounds of polymeric MDI, it now meets the 25,000-pound threshold for reporting, and the release of both chemicals must be reported as a cumulative number. The requirement to aggregate exists for all isocyanates in the category. Formerly, only MDI releases were reported, and processing the above amounts would not meet the threshold for reporting.

Almost all facilities in the polyurethane industry process or use PMDI rather than pure MDI. PMDI is typically used as a mixture of MDI, a solid at ambient temperatures, dissolved in polymeric MDI, which is a liquid. Polymeric MDI has a lower vapor pressure than pure MDI. Consequently, MDI/PMDI mixtures have lower vapor pressures than pure MDI, and release estimates that were based in the past on the vapor pressure of pure MDI often significantly overstated emissions - particularly air release estimates. In response to the addition of the diisocyanates category to the EPCRA reporting requirement, these guidelines provide a means of adjusting emission estimates to reflect more accurately the possible releases from facilities that use MDI/PMDI mixtures. This workbook, however, does not provide guidance on estimating emissions of other isocyanates included in the diisocyanate category. Check with your supplier and your own technical or legal advisors for assistance.

EPCRA Overview

To put the Section 313 requirements in perspective, this chapter very briefly reviews the provisions of the Emergency Planning and Community Right-to-Know Act (EPCRA), and the Pollution Prevention Act (PPA). Additional materials addressing EPCRA requirements are available from the Alliance for the Polyurethanes Industry (API).

EPCRA, also known as Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA), was enacted on October 17, 1986. EPCRA has four major sections: emergency planning (Section 301-303), emergency release notification (Section 304), hazardous chemical inventory reporting requirements (Section 311-312), and toxic chemical release reporting/emissions inventory (Section 313). A summary of these sections follows.

Section 301-303: Emergency Planning

The emergency planning provisions of EPCRA are specifically designed to allow for emergency response and preparedness through coordination and planning at the state and local level. The concept involves a multi-tiered system capable of coordinating emergency activities. The governors of each state must designate a state emergency response commission (SERC), which, in turn, must designate local emergency planning districts (LEPD), and appoint local emergency planning committees (LEPC). SERCs are responsible for supervising and coordinating the activities of the LEPCS, for establishing procedures for receiving and processing public requests for information, and for reviewing local emergency plans. These commissions and committees are required to

have broad representation from the public and the private sector, including community groups, representatives of the media, and representatives of facilities subject to emergency planning requirements. The LEPCs must develop emergency response plans that meet minimum criteria.

Section 304: Emergency Release Notification

Any time there is a release of a listed CERCLA hazardous substance (*see* 40 CFR Section 302.4) or an EPCRA extremely hazardous substance (*see* 40 CFR Part 355) that exceeds the reportable quantity (R.Q.) for that substance, the facility must immediately notify the LEPC, SERC and National Response Commission (NRC). In addition to following the notification requirements, the facility must submit a follow-up written emergency notice that sets forth the actions taken to respond to the release and any risks posed by the incident.

Section 311-312: Hazardous Chemical Inventory Reporting

The chemical inventory reporting requirements under EPCRA Sections 311 and 312 apply to manufacturers, importers, processors, and users of substances for which material safety data sheets (MSDS) must be maintained under the Occupational Safety and Health (OSH) Act. Under EPCRA Section 311, such facilities must prepare or have available MSDS's and submit either copies of the MSDS's or a list of the hazardous chemicals to the LEPC, SERC, and local fire department if more than a threshold level is stored onsite at any one time (*see* 40 CFR Section s 370.20-.28).

The threshold level varies depending on how the chemical is classified. For hazardous chemicals that are not extremely hazardous substances (EHS), the threshold is 10,000 pounds. On the other hand, if the hazard chemical is also an EHS (listed in 40 CFR Part 355, Appendices A and B), the reporting threshold is 500 pounds or that chemical's threshold planning quantity (TPQ), whichever is lower.

Section 312 requires an annual submission of an emergency and hazardous chemical inventory form, known as the Tier One or Tier Two Report, to the LEPC, SERC and local fire department (*see* 40 CFR Sections 370.40-.41).

Section 313: Toxic Chemical Release Reporting/Emissions Inventory

As noted above, EPCRA Section 313 requires affected facilities to provide information on routine and accidental releases of specific chemicals, among other things. A "release" includes vaporization or discharge of the chemical into the air, discharge of the chemical into a sewage system, and disposal of the chemical in landfills, either directly or via a waste management contractor.

10 full-time employees = 20,000 hours of work in a year. Add the hours worked by **all employees** during the calendar year, including the hours worked by contract employees, part-time employees, and sales and support staff. Divide by 2,000, if the resulting number is greater than 10, the criterion has been met.

Section 313 of EPCRA requires that a report be filed by an owner and/or operator of a facility that meets all of the following criteria:

- The facility has the equivalent of 10 or more full-time employees; and
- The facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20-39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under the RCRA Subtitle C, 42 U.S.C. section 6921 *et seq.)*, 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and

- The facility manufactures (defined to include importing), processes, or otherwise uses any EPCRA Section 313 chemical in quantities greater than the established threshold in the course of a calendar year.

See 40 CFR Section 372.22 for further explanation of when a facility falls within a listed SIC code. Reporting documents, including the Form R and Form A, may be accessed at http://www.epa.gov/tri/report/index.htm.

Form R Toxic Release Inventory Reporting Form

Facilities that are subject to the requirements of Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 are required to file a Form R for each EPCRA chemical for which the applicable threshold limits are exceeded. (An exception is that, if certain low use/low emission criteria are met, the facility may be able to submit a Form A rather than a Form R – see below.)

Form R consists of two parts:

- Part 1: Facility Identification Information
- Part II: Chemical-Specific Information

The Facility Identification Information that must be provided in Part I of Form R includes five sections:

- Section 1. Reporting Year
- Section 2. Trade Secret Information
- Section 3. Certification
- Section 4. Facility Identification
- Section 5. Parent Company Information

The Chemical-Specific Information that must be provided in Part II of Form R includes eight sections that must be completed for each listed EPCRA chemical that meets the reporting criteria. The sections are:

- Section 1. Toxic Chemical Identity
- Section 2. Mixture Component Identity
- Section 3. Activities and Uses of the Toxic Chemical at the Facility
- Section 5. Quantity of the Toxic Chemical Entering Each Environmental Medium Onsite
- Section 6. Transfers of the Toxic Chemical in Wastes to Off-Site Locations
- Section 7 On-Site Waste Treatment Methods – Energy Recovery Processes – Recycling Process
- Section 8. Source Reduction and Recycling Activities

This document is intended to provide guidance that will enable processors or users of MDI and MDI/PMDI mixtures to estimate air releases of these chemicals for purposes of completing Part II, Section 5 of Form R. Information regarding the filing of Form R, frequently asked questions, filing software, forms, etc. can be obtained on the TRI Home Page (http://www.epa.gov/tri) or the TRI Guidance Documents Page (http://www.epa.gov/tri/guide_docs/index.htm.

Form A Certification Statement Introduced

In 1994, EPA established the Form A Certification Statement – known as Form A -- to simplify and reduce the compliance burden associated with EPCRA Section 313. Like the Form R, Form A must be submitted annually, but instead of a five-page report, the Form A consists of only two pages. Part I requires facility identification information, and Part II requires information on the toxic chemical's identity.
A facility may submit a Form A rather than a Form R if --

(1) The total annual reportable amount for the toxic chemical does not exceed 500 pounds; and

(2) The facility does not manufacture, process or otherwise use greater than 1 million pounds of the toxic chemical.

The Form A, however, should not be used for the reporting of any PBT chemical, as identified under 40 CFR Section 372.28.

The "total annual reportable amount" is equal to the combined total quantities of the toxic chemical released at the facility, disposed within the facility, treated at the facility (as represented by amounts destroyed or converted by treatment process), recovered at the facility as a result of recycle operations, combusted for the purpose of energy recovery at the facility, and amounts transferred from the facility to off-site locations for the purpose of recycle, energy recovery, treatment, and/or disposal. These volumes correspond to the sum of amounts reported on the Form R, section 8 (data elements 8.1 through 8.7).

Since 1998, Form A may be used to report up to four chemicals that meet the criteria listed above. If more than four chemicals meet the criteria, they may be listed on additional copies of Part II: Chemical Identification (page 2). A complete report for Form A consists of at least two pages for each submission. Reporting documents, including the Form A, may be accessed at http://www.epa.gov/tri/report/index.htm.

Pollution Prevention Act of 1990

The Pollution Prevention Act of 1990 (PPA) requires facilities subject to the reporting requirements of EPCRA Section 313 to provide information concerning pollutant source reduction and recycling activities. Pollution prevention information must be included with the annual section 313 Toxic Chemical Release "Form R."

On May 27, 1992, EPA published revisions to the Form R, incorporating required pollution prevention information. Mandatory source reduction and recycling activity information and detailed information regarding on-site waste treatment and recycling must be reported.

The PPA requires reporting of the following information:[1]

1. The quantity of each reportable chemical entering any waste stream prior to recycling, treatment, or disposal;

2. The amount of each chemical from the facility which is recycled, including the percentage change from the previous year and the process of recycling used;

3. Source reduction practices used with respect to each chemical for each of the following categories:

    a. Equipment, technology, process, or procedure modifications;

[1] The PPA should be consulted for the exact language of the reporting requirements.

b. Reformulation or redesign of products;

c. Substitution of raw materials;

d. Improvements in management and operations;

4. The projected quantity of each chemical recycled for two calendar years immediately following the reporting year;

5. A ratio of production (or other activity) in the reporting year to production (or other activity) in the previous year that adequately characterizes the primary influence on the quantity of a toxic chemical entering wastes;

6. Techniques that were used to identify source reduction opportunities;

7. The amount of any toxic chemical released into the environment which results from a catastrophic event; and

8. The amount of any reportable chemical that is subject to treatment (other than in-process source reduction or recycling) during any calendar year and the percentage change from the previous year.

A challenging element for companies reporting pollution prevention information is developing production ratio/activity indices for operations. The production ratio is intended to reflect the extent to which year-to-year changes in release estimates are due to source reduction activities versus changes in business activity. Companies are currently free to identify the most appropriate methods or activities on which to base production ratios for each chemical. This may be a difficult task for facilities that may use section 313 chemicals in many different operations.

Are You Subject to EPCRA Reporting Obligations?

A general decision tree for determining if you must report releases under section 313 of EPCRA is provided on the front cover of this document. This section of the booklet expands upon the questions in the decision tree by summarizing the general steps that must be taken to determine if you must report releases of MDI, MDI and polymeric MDI mixtures and other section 313 listed chemicals that you manufacture, process, or use.

Is Your Facility Subject to Section 313 Reporting?

Section 313 reporting requirements apply to facilities in Standard Industrial Classification (SIC) Codes 20-39, among others. SIC Codes 20-39 include chemical manufacturers, plastic resin, foam, and other plastic product manufacturers, foundries, boat builders, and automotive and recreational vehicle manufacturers. ***Foam contractors who install foam insulation in houses or businesses or by spraying polyurethane on-site are NOT subject to reporting at this time.*** Be aware, however, that this could change in the future, so these requirements need to be monitored.

Do You Manufacture, Process or Otherwise Use MDI, PMDI or Other Substances That Are On the Section 313 List?

Both 4,4'-methylene diphenyl diisocyanate (4,4'-MDI or MDI) and polymeric MDI (PMDI) are included in the diisocyanate category. 4,4'-MDI is identified by Chemical Abstract Services (CAS) Registry Number (RN) 101-68-8 and should be aggregately reported with other isocyanates in Category N120. Synonyms for MDI are provided in Table 1.

Table 1
Synonyms for MDI

1,1'-methylenebis [4-isocyanato benzene]
bis(4-isocyanatophenyl) methane
diphenylmethane 4,4'-diisocyanate
methylenebis (4-isocyanatobenzene)
MBI
4,4'-MBI
isocyanic acid, methylenedi-p-phenylene ester
bis(p-isocyanatophenyl) methane
p,p'-methylenebis (phenyl isocyanate)
4,4'-methylenebis (phenyl cyanate)
methylenebis (4-phenyl isocyanate)
methylenedi-p-phenylene diisocyanate
methylenebis (4-phenylene isocyanate)
methylenedi-p-phenylene isocyanate
4,4'-diisocyanatodiphenylmethane
methylenebis(p-phenylene isocyanate)
methylenebis (p-phenyl isocyanate)
bis (1,4-isocyanatophenyl) methane
methylenebis-p-phenylene diisocyanate
4,4'-methylenediphenylene isocyanate
4,4'-diphenylmethane diisocyanate
p,p'-diphenylmethane diisocyanate
4,4'-methylenedi-p-phenylene diisocyanate
diphenylmethane diisocyanate
di(4-isocyanatophenyl) methane
diphenylmethylene diisocyanate
4,4'-methylenebis(isocyanatobenzene)
methylenebisphenylene diisocyanate
isocyanic acid, diphenylmethylene ester

The most widely used MDI/PMDI mixture consists of approximately 50% monomeric 4,4'-methylene diphenyl diisocyanate (MDI, CASRN 101-68-8) -- which was on the Section 313 list even before EPA promulgated the November 1994 rule - and 50% higher molecular weight oligomers (PMDI, CASRN 9016-87-9) of variable composition.[2] This MDI/PMDI mixture generally exists as an amber, viscous liquid at ambient temperatures. As

[2] 59 Fed. Reg. 61,432 (November 30, 1994).

described in the discussion above, MDI and PMDI are aggregated with other isocyanates for TRI reporting. Only a single cumulative quantity is reported using the diisocyanates Category Code N120. *Please note that* individual CAS Registry Numbers should NOT be used when reporting under Category Code N120.

Users and processors must report releases of all chemicals in any listed category listing as a single number. *Different estimation techniques will likely be needed for the various members of the diisocyanates category. This book provides guidance on MDI and PMDI only.* Table 2 lists all the isocyanates in the category. ***Please note*** that TDI is not a member of the diisocyanates category, and that release estimates for TDI should be reported separately.

Table 2
Isocyanates in the Section 313
Diisocyanates Reporting Category
Category Code N120

Chemical Name	**CASRN**
Methylene*bis* (phenyl isocyanate) (MDI)	101-68-8
1,3-Bis(methylisocyanate)-cyclohexane	38661-72-2
1,4-*bis*(Methylisocyanate)cyclohexane	10347-54-3
1,4-Cyclohexane diisocyanate	2556-36-7
Diethyldiisocyanatobenzene	134190-37-7
4,4'-Diisocyanatodiphenyl ether	4128-73-8
2,4'-Diisocyanatodiphenyl sulfide	75790-87-3
3,3'-Dimethoxylbenzidine-4,4'-diisocyanate	91-93-0
3,3'-Dimethyl-4,4'-diphenylene diisocyanate	91-97-4
3,3'-Dimethyl diphenylmethane-4,4'-diisocyanate	139-25-3
Hexamethylene-1,6-diisocyanate	822-06-0
Isophorone diisocyanate	4098-71-9
4-Methyldiphenylmethane-3,4-diisocyanate	75790-84-0
1,1-Methylene*bis*(4-isocyanatocyclohexane)	5124-30-1
1,5-Naphtalene diisocyanate	3173-72-6
1,3-Phenylene diisocyanate	123-61-5
1,4-Phenylene diisocyanate	104-49-4
Polymeric diphenylmethane diisocyanate (PMDI)	9016-87-9
2,2,4-Trimethylhexamethylene diisocyanate	16938-22-0
2,4,4-Trimethylhexamethylene diisocyanate	15646-96-5

There are other section 313 chemicals that may also be used in your process as blowing agents, catalysts, polyols and additives. A list of other section 313 listed substances that are commonly used with MDI is provided in Table 3. **This is not an exhaustive list.** Please consult the most recent year's TRI reporting list, which is updated yearly and printed in the "TRI Reporting Form R and Instruction" book, for a complete list of substances for which Section 313 reporting may be required. The TRI reporting list may be accessed at http://www.epa.gov/tri/report/index.htm. The list of TRI reportable chemicals is also in the Code of Federal Regulations at 40 C.F.R. § 372.65.

Table 3
Other Section 313 Chemicals Commonly Used by the Polyurethane Industry

Additive Type/Chemical Name	CASRN
Diisocyanates	
Toluene-2,4-diisocyanate	584-84-9
Toluene-2,6-diisocyanate	91-08-7
Toluene diisocyanate (mixed isomers)	26471-62-5
Curing Agents	
Ethylene glycol	107-21-1
Certain glycol ethers	category
Diethanolamine	111-42-2
Catalysts	
Lead compounds	category
Mercury compounds	category
Fillers	
Barium compounds (except barium sulfate)	category
Colorants	
Cadmium compounds	category
Cobalt compounds	category
Copper compounds (excluding certain phthalocyanine-based pigments)	category
Solvents	
Toluene	108-88-3

Do You Manufacture, Process or Otherwise Use Greater Than a Threshold Amount of Any Section 313 Chemical?

"Manufacture:" to produce, prepare, compound or import a listed toxic chemical, including the coincidental production of a toxic chemical (*e.g.*, as a by product or impurity).

"Process:" preparation of a listed toxic chemical, after its manufacture, for distribution in commerce (*e.g.*, the intentional incorporation of the chemical into a product).

"Otherwise use:" any activity involving a listed toxic chemical that does not fall within the definition of "manufacture" or "process."

Application of the TRI reporting requirements is based on whether a facility manufactures processes or otherwise uses greater than a threshold amount of a listed chemical. Historically, if you met the requirements above, and either (1) manufactured or processed more than 25,000 pounds of a listed chemical or chemical category, or (2) otherwise used more than 10,000 pounds of a listed chemical or chemical category, you had to comply with the EPCRA reporting requirements.[3]

In 1999, however, EPA created a subset of listed chemicals, known as persistent and bioaccumulative toxic (PBT) chemicals that are subject to lower thresholds. Dioxin and dioxin-like compounds that are subject to a 0.1 gram threshold; other listed PBTs are subject to either a 10 pound or 100 pound threshold for amounts manufactured, processed or otherwise used (*see* 40 CFR Section 372.28). A list of PBTs and their thresholds is provided as Table

Table 4
List of PBTs

Chemical Name	Cas No./ Category Code	Threshold Limit
Benzo(g,h,I)perylene	00191-24-2	10 lbs.
Octachlorostyrene	29082-74-4	10 lbs.
Pentachlorobenzene	00608-93-5	10 lbs.
Tetrabromobisphenol A	00079-94-7	100 lbs.
Vanadium Compounds	N770	1 lb.
Aldrin	309-00-2	100 lbs.
Chlordane	57-74-9	10 lbs.
Dioxin and Dioxin-like Compounds	N150	0.1 gram
Heptachlor	76-44-8	10 lbs.
Hexachlorobenzene	118-74-1	10 lbs.
Isodrin	465-73-6	10 lbs.
Lead	7439-92-1	100 lbs.
Lead Compounds	N420	100 lbs.
Mercury	7439-97-6	10 lbs.
Mercury Compounds	N458	10 lbs.
Methoxychlor	72-43-5	100 lbs.
Pendimethalin	40487-42-1	100 lbs.
Polychlorinated bisphenyls (PCBs)	1336-36-3	10 lbs.
Polycyclic Aromatic Compounds (PACs)	N590	100 lb.
Tetrabromobisphenol A	79-94-7	100 lbs.
Toxaphene	8001-35-2	10 lbs.
Trifluralin	1582-09-8	100 lbs.

[3] The reporting threshold for Sections 311/312 of EPCRA should be distinguished from the Section 313 threshold. Under Sections 311/312, you are required to file an MSDS and annual inventory reports with state and local agencies if you store MDI on site in quantities greater than 10,000 pounds at any one time.

Note:

For a complete listing of chemicals found in the listed categories consult EPA's "Section 313 of the Emergency Planning and Community Right-to Know Act Toxic Chemical Release Inventory Reporting Forms and Instructions Revised 2002 Version", United States Environmental Protection Agency, March 2003, *available at* http://www.epa.gov/tri/report/rfifinal2002603.pdf.

The 25,000 pounds manufacturing and processing and 10,000 pounds otherwise use thresholds, however, still apply to the diisocyanates category.

The 25,000 pound threshold will apply to most MDI and MDI/PMDI "users" since most applications, including polyurethane foam manufacturing and use in boat building, are considered to involve "processing" for purposes of section 313 reporting. EPA considers utilization of MDI-based products in making foundry molds that are used on-site and are not distributed in commerce as a "otherwise use" of MDI and MDI/PMDI mixtures for section 313 reporting. In such applications, the 10,000-pound reporting threshold applies.

Your purchases of section 313 listed chemicals may serve as a benchmark in determining what amounts you manufacture, process, or "otherwise use"; however, it is the actual amount of a substance that is manufactured, processed, or "otherwise used" in the reporting year that determines your reporting status. For example, a facility that purchased 30,000 pounds of MDI, a listed chemical, but processed only 24,000 pounds in the reporting year would not be required to report. Alternatively, a facility that purchased and processed 20,000 pounds of MDI and processed an additional 6,000 pounds from the previous year's inventory, thereby processing a total of 26,000 pounds in one reporting year, would be required to report.

For chemicals like MDI and PMDI that are included in a category, the reporting threshold is based on the sum of **all** of the chemicals in the category processed or used in the reporting year. Thus, reporters must count all of the isocyanates manufactured, processed or "otherwise used" in the category in that reporting year in determining if a threshold is met.

If you have a mixture or trade name product that contains a toxic chemical, you must determine the amount of the toxic chemical in the mixture and combine that amount to the total quantity of the chemical processed or otherwise used at the facility in order to determine whether or not the reporting threshold has been reached.

EXAMPLE

		Otherwise using:	
Mixture 1:	10,000 pounds	Mixture 2:	12,000 lbs
Components:	50% water	Components:	50% water
	50% MDI		50% Isophorone diisocyanate

Conclusion: Exceeds the reporting threshold for the diisocyanates category.
You used 5,000 lbs of MDI and 6,000 lbs of Isophorone diisocyanate. Because the total amount of diisocyanates exceeds the 10,000 pound "otherwise used" threshold, you must file a TRI Report.

Are You Subject to State MDI Permit Reporting Obligations?

If a mixture of MDI and PMDI is processed or used (which is almost always the case), the combined emissions of both substances should be reported under section 313. (In contrast, state air permit officials may be particularly interested in MDI emissions alone, because MDI is a listed hazardous air pollutant (HAP).) The estimation techniques in this book are directed primarily toward calculating emissions for the purpose of Section 313 reporting but may be useful in providing MDI emission estimates for state permitting purposes as well.

Table 4
List of PBTs

Chemical Name	Cas No./ Category Code	Threshold Limit
Benzo(g,h,I)perylene	00191-24-2	10 lbs.
Octachlorostyrene	29082-74-4	10 lbs.
Pentachlorobenzene	00608-93-5	10 lbs.
Tetrabromobisphenol A	00079-94-7	100 lbs.
Vanadium Compounds	N770	1 lb.
Aldrin	309-00-2	100 lbs.
Chlordane	57-74-9	10 lbs.
Dioxin and Dioxin-like Compounds	N150	0.1 gram
Heptachlor	76-44-8	10 lbs.
Hexachlorobenzene	118-74-1	10 lbs.
Isodrin	465-73-6	10 lbs.
Lead	7439-92-1	100 lbs.
Lead Compounds	N420	100 lbs.
Mercury	7439-97-6	10 lbs.
Mercury Compounds	N458	10 lbs.
Methoxychlor	72-43-5	100 lbs.
Pendimethalin	40487-42-1	100 lbs.
Polychlorinated bisphenyls (PCBs)	1336-36-3	10 lbs.
Polycyclic Aromatic Compounds (PACs)	N590	100 lb.
Tetrabromobisphenol A	79-94-7	100 lbs.
Toxaphene	8001-35-2	10 lbs.
Trifluralin	1582-09-8	100 lbs.

Note:

For a complete listing of chemicals found in the listed categories consult EPA's "Section 313 of the Emergency Planning and Community Right-to Know Act Toxic Chemical Release Inventory Reporting Forms and Instructions Revised 2002 Version", United States Environmental Protection Agency, March 2003, *available at* http://www.epa.gov/tri/report/rfifinal2002603.pdf..

When, Where and How Should the TRI Reporting Data be Sent?

As specified in EPCRA Section 313, the report for any calendar year must be submitted on or before July 1 of the following year whether using Form R or Form A. If the reporting deadline falls on a Saturday or Sunday, EPA will accept reports the are postmarked on the following Monday. Any voluntary revision to a report can be submitted anytime during the calendar year for the current or any previous reporting year. However, voluntary revisions for the current reporting year should be submitted by July 31 in order to be included in that year's public data release.

Submissions must be sent to both EPA and the State or the designated official of an Indian tribe. If a report is not received by both the EPA and the State or designated official of an Indian tribe, the submitter is considered out of compliance and subject to enforcement action. Send reports to EPA by regular mail to:

TRI Data Processing Center
P.O. Box 1513
Lanham, MD 20703-1513
Attn: Toxic Chemical Release Inventory

Certified mail or overnight and hand-delivered submissions only should be addressed to:

TRI Data Processing Center
C/o Computer Sciences Corporation
Suite 300
8400 Corporate Drive
New Carrollton, MD 20785
301 429-5005

Also send a copy of the report to the state in which the facility is located. A directory of state TRI program contacts and web sites is available at http://www.epa.gov/tri/programs/state_programs.htm. Facilities located on Indian land should send a copy to the Chief Executive Officer of the applicable Indian tribe. Some tribes have entered into a cooperative agreement with states: in this case; a report submission should be sent to the entity designated in the cooperative agreement.

There are three ways in which the Toxic Release Inventory reports can be submitted. Reports can be submitted by magnetic media, via the Internet, and/or paper submittal. The EPA has developed a package called "TRI Reporting Software". This easy-to-use CD-ROM includes ATRS and TRI-ME software and comes with complete instructions for its use. It also provides prompts and messages to help you report according to EPA instructions. If reports are being filed by magnetic media or diskette, you must enclose a cover letter signed by the official; listed in Section 3 of Part 1 of the Form R or Form A (name and official title of owner/operator or senior management official) for each separate facility. Under no circumstances, if filling by diskette, do you include a paper copy.

Copies of the CD-ROM can be obtained by calling EPA at (202) 564-9554 or downloading from the EPA website located at http://www.epa.gov/tri.

Note Some States may not accept magnetic media or computer-generated facsimile reports.

Form R and/or Form A can also be submitted via the Internet to EPA's Central Data Exchange. The TRI-ME software has the ability to directly submit your TRI submissions via the internet; however, if you choose to submit your TRI Form R's and /or Form A's by the Internet, you also must send a certification letter signed by the official listed in Section 3 of Part 1 of the Form R and /or Form A for each facility being reported. Once the submission has been successfully submitted via the Internet, TRI-ME will prompt you to print your certification letter. It is important to use the certification letter printed from the software because it will contain your CDX identification number, which is a unique identifier in matching your certification letter with the data that you submitted.

Note that submitting your Form R's and/or Form A's via the internet does not in any way satisfy your state requirements, and remember that not all states except electronic submittals.

What Kinds of Records Should be Maintained and for How Long?

Sound record keeping practices are essential for accurate and efficient TRI reporting. It is in the facility's interest, as well as, EPA's, to maintain records properly.
A partial list of records, organized by year, that a facility should maintain includes:

- Previous years' EPCRA Section 313 Reports
- EPCRA Section 313 Reporting Threshold Worksheet
- Engineering Calculations and other Notes
- Purchase Records from Suppliers
- Inventory Data
- EPA (NPDES) Permits and Monitoring Reports
- EPCRA Section 312 Tier II Reports
- Monitoring Reports
- Flowmeter Data
- RCRA Hazardous Waste Generator's Report
- Pretreatment Reports filed with Local Government
- Invoices from Waste Management Companies
- Manufacturer's Estimates of Treatment Efficiencies
- RCRA Manifests
- Process Diagrams that Indicates Emissions and other Releases
- Records for those EPCRA Section 313 Chemicals for which they did not file EPCRA Section 313 Reports

For at least 3 years from the date of submission, facilities must keep a copy of each report filed, along with the supporting documents (*see* 40 CFR Section 372.10). These reports will be helpful in completing future reports. They will also be required in the event that EPA requests documentation to support the data elements reported on a facility's Form A or Form R.

EPA may conduct data quality reviews of Form R or Form A submissions. An essential component of this process involves the reviewing a facility's records for accuracy and completeness.

How Do I Revise or Withdraw TRI Data?

Facilities that have filed a Form R and/or Form A Certification under EPCRA Section 313 may find it necessary to revise or withdraw TRI data. In order to have a submission in the TRI database **revised** a facility must submit a request to both EPA and the appropriate State Agency by submitting a 'Request for Revision' template and a copy of the Form R or Form A Certification that has to be revised. A copy of this template can be found in Appendix H-1, in the TRI Reporting Forms and Instructions, or at http://www.epa.gov/tri/guide_docs/2002/rev_wthdrl.pdf.

In order for the EPA to effectively process the request, EPA needs the following information:

- Facility Name and TRI Identification Number (TRIFID)
- Facility Mailing Address
- Reporting Year
- Chemical Name
- Technical Contact name and Telephone Number
- Name and Telephone Number of Requester
- Reason(s) for Revision
- Signature

Some of the key reasons for submitting a request for revision are:

- Revision of Facility Identification Information
- Revision of Chemical Identification Information
- Revision of Release and other Waste Management Activities Information
- Result of an EPA/State Inspection
- Result of Notice of Technical Error, Notice of Significant Error, or Notice on Noncompliance from EPA
- Result of Voluntary Disclosure or Audit Policy

Hardcopy revisions may be submitted using the most recent form available or the most recent version of the ATRS or TRI-ME software. Certify and date the form on page 1 or provide a cover letter with the software created data revision. Alternatively, you may also submit a photocopy of your original submission (from your file) with the corrections made in blue ink. Re-sign and date the certification statement on page 1. **Whenever you submit a diskette, do not submit a printout of what is on the diskette, because both the diskette and the printout will be processed as separate submissions, potentially resulting in duplicate records for your facility.**

Facilities that wish to request to the EPA to **withdraw** the Form R and/or Form A Certification submissions from EPA's database must submit a 'Request for Withdrawal' template to the EPA and the state agency along with a copy of the Form R or Form A certification they wish to have withdrawn. EPA will review each request and notify the requestor by letter whether or not the withdrawal request has been accepted. The information that needs to be submitted is similar to that listed above in "Request for Revision."

Some of the key reasons for requesting withdrawal are:

- The facility manufactures, processes or otherwise uses less than the threshold quantities
- Change in EPA's reporting requirements for a chemical
- The facility qualifies for EPCRA Section 313 exemptions
- The chemical reported is not an EPCRA Section 313 reportable chemical
- The chemical reported in not in the form listed on the EPCRA Section 313 Toxic Chemical List (i.e., aerosol, fume or dust, fibrous form, etc.)
- Activities involving the reported chemical do not meet EPA's definition of "manufacture, process or otherwise use"
- The facility qualifies for a Form A Certification Submission

Where do you Send Requests for Revision or Withdrawal of Data?

TRI Form R and/or Form A **revision requests** should be sent to the EPCRA Reporting Center.

If sending by regular U.S. mail, send to:

Toxics Release Inventory (TRI) Data Processing
P.O. Box 1513
Lanham, MD 20703-1513
Attention: TRI Revision Request

If sending by certified mail or overnight mail:

TRI Data Processing Center
C/o Computer Sciences Corporation
Suite 300
8400 Corporate Drive
New Carrollton, MD 20785
Attention: TRI Revision Request

Withdrawal requests for TRI Form R and/or Form A Certification should be sent to the EPCRA reporting center.

If sending by regular U.S. mail, send to:

Toxic Release Inventory (TRI) Data Processing
P.O. Box 1513
Lanham, MD 20703-1513
Attention: TRI Withdrawal Request

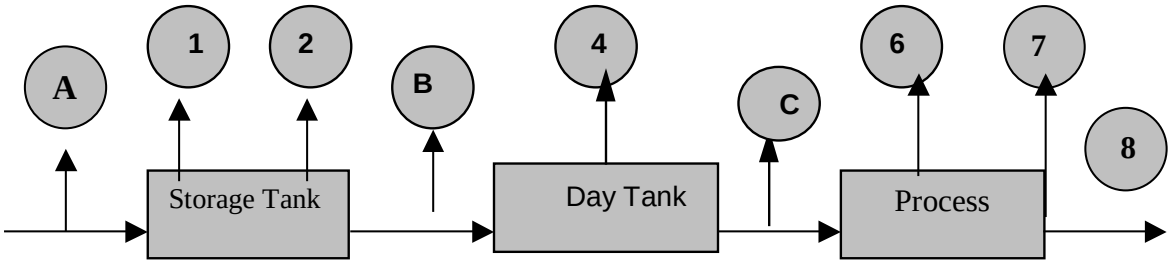
If sending by certified mail or overnight:

TRI Data Processing Center
C/o Computer Sciences Corporation
Suite 300
8400 Corporate Drive
New Carrollton, MD 20785
Attention: TRI Withdrawal Request

Identifying Release Sources

The main goal and objective of this document is to provide information and guidance that will enable processors or users of MDI and MDI/PMDI mixtures to estimate releases of these chemicals in accordance with the Emergency Planning and Community Right to Know Act (EPCA) Section 313.

The first step in estimating the release of MDI and/or MDI/PMDI mixtures is to identify all possible emission sources. To do this, it may be helpful to develop a process flow diagram, outlining and depicting the activities in which MDI and MDI/PMDI emissions can be released. A general plant flow diagram presented below provides a broad overview of where emissions can occur and will be used to outline the general approach in calculating emissions throughout this document.



A **Transfer from Tanker or Railcar**

1 **Working Losses**

2 **Breathing Losses**

B **Transfer from Storage Tank to Day Tank**

8 **Disposal and Treatment**

4 **Tank Breathing Losses**

C **Transfer to Process**

6 **Process Stack Losses**

7 **Fugitive Emissions**

Once the activities have been identified for your facility, a systematic approach to calculating your overall emissions can be established. Each facility is unique and even though the regulation does not require you to generate a process flow diagram, preparation of a process flow diagram can and will demonstrate your efforts to responsibly comply with the EPCA reporting requirements

Estimating Releases of MDI and PMDI

Techniques:

Once all the possible release sources for MDI or MDI/PMDI mixtures have been identified, estimates of the quantity released from each source can be made.

Section 313 requires all releases to air, water, land, and transfers to off-site facilities for each toxic chemical meeting the threshold reporting requirements be reported.

In general, there are four basic techniques used to estimate emissions.

- Direct Measurement
- Mass Balance
- Emission Factors
- Engineering Calculations

The following section summarizes each basic technique that can be used to determine emissions. It may become necessary to employ a combination of all these techniques to obtain the total amount of estimated emissions for your facility.

Direct Measurement:

The use of direct measurement or monitoring data to determine release measurement is based upon measured concentrations of a chemical in a waste stream and the flow rate/volume of that stream. Direct measurement gives you a more accurate account of what amounts of chemicals is being released. Even though this method is very costly than using other estimation techniques, this additional effort can be justified in instances where other estimation techniques may significantly overestimate releases. Direct data measurement consists of stack monitoring data, process equipment bagging studies, and waste stream contaminant analysis data. Industrial hygiene data is useful for evaluating worker exposure and estimating fugitive emissions, but should not be used in estimating process releases.

Mass Balance:

The use of mass balance to determine release estimates are based upon the assumption that the amount of chemical entering the process must be the same as the amount of chemical that leaves the process. If the input and output streams for a particular process are known, the difference would be the amount of material that is lost through waste streams, stacks, and as fugitives. **However, using mass balance is inappropriate to use in situations where a chemical is consumed during a process were the chemical goes under a chemical reaction with another chemical to form a new compound.** It is also inappropriate to use mass balance in situations where a chemical is destroyed by heat or combustion. Nearly all applications that use MDI and MDI/PMDI fall into this category. When a two part MDI-based polyurethane system is used, the MDI/PMDI is converted to a polyurethane polymer and is not present in the final product other than as a residual.

Emission Factors:

Emission factors express releases as a ratio of the amount of a substance released relative to process or equipment throughput. Emission factors are commonly used for air releases and are typically based upon the average measured emissions measured at several facilities in the same industry. The EPA has compiled a large number of emission factors for different chemicals used in many industries. However there is very little emission factor data available for MDI and MDI/PMDI mixtures. Consequently, use of EPA emission factors could result in over-reporting.

Engineering Calculations:

Engineering calculations are assumptions and/or judgments used to estimate quantities of EPCA Section 313 chemicals and chemical categories released or otherwise managed as waste. The quantities are estimated by using physical and chemical properties and relationships (e.g., ideal gas law, Raoult's law, Henry's law) or by modifying an emission factor to reflect the chemical properties of the chemical in question. Engineering calculations rely on the process parameters; you must have a thorough knowledge of your facility operations to complete these calculations. For example, in estimating releases from closed mold-type processes, knowledge about the relationship between vapor pressure, temperature, and volume is used to calculate the maximum amount of MDI or MDI/PMDI that can be released from a single mold filling activity. Multiplying the amount that can be released or emitted per mold and multiplying by the number of molds fillings that occur in a given year provides a reasonable estimate of annual releases for that operation.

Engineering calculations can also include computer models. Several computer models are available for estimating emissions from stacks, landfills, wastewater treatment, water treatment and other processes.

Non-chemical-specific emission factors, Synthetic Organic Chemicals Manufacturing Industry (SOCMI) emission factors, industry-determined emission factors for processes or equipment, and site-specific emission factors also can be used, but must be classified as "Engineering Calculations" for EPCRA Section 313 reporting.

Simplified estimation techniques have been employed throughout the guideline document to make estimations of releases understandable. Adjustment factors are provided where MDI/PMDI mixtures are processed or used to calculate the combined emissions of both substances. The adjustment factors have been derived using actual measurement data on the vapor pressure for a range of MDI/PMDI mixtures. The emissions from processing or use of MDI/PMDI mixtures are always lower than emissions from the same activities where pure MDI is employed.

In estimating releases from facilities that use MDI/PMDI mixtures, emissions are first calculated as if MDI comprises 100 per cent of all mixtures and then an adjustment factor is used based upon the content of MDI in the mixture.

General equations and assumptions are used repeatedly throughout the guidebook. These assumptions are intended to provide conservative or reasonable worst-case assessments in estimating potential MDI and MDI/PMDI releases. Examples in the guidebook were selected to reflect major scenarios where releases are likely to occur. There may be release scenarios particular to your facility that is not described in this guidebook. The best judge of the use of any release source or release estimation technique is always an individual with knowledge of a specific operation at your facility. **Do not use the estimation techniques that follow if you feel that they are not based on assumptions that reflect your facility's operation.**

A more descriptive account of these techniques is provided in the U.S. EPA publication***, "Estimating Releases and Waste Treatment Efficiencies for the Toxic Chemical Release Inventory Forms"*** *(1999 edition Reference 1).*

U.S. EPA does not require you to conduct additional sampling or testing for EPCRA Section 313 reporting, however, you are required to use the best, readily available information to determine the method that will result in the most accurate estimate.

Tables I list the potential data source where available release and emission information may be obtained to help in determining accurate facility emissions.

Table I: Potential Data Sources for Release and Other Waste Management Calculations

Monitoring Data

* Air Permits
* Continuous Emission Monitoring
* Effluent Limitations
* Hazardous Waste Analysis
* Industrial Hygiene Monitoring Data
* NPDES Permits
* Stack Monitoring Data

Mass Balance

* Air Emissions Inventory
* MSDS's
* Pollution Prevention Reports
* Spill Event Records
* Supply Records
* Hazardous Waste Manifests

Engineering Calculations

* Facility Non-specific Emission Factors
* Henry's Law
* Raoult's Law
* Solubilities
* Volatilization Rates

Emission Factors

* AP-42 Chemical Specific Emission Factors
* Facility or Trade Association Derived Chemical Factors

General, Chemical-Specific, and Industry-Specific Guidance Documents

EPA has a number of EPCRA Section 313 documents that provide information and guidance to help assist one in completing and filing Form R and Form A Certification Documents. It is recommended that one obtain and read these documents before starting to fill out the forms. The Guidance Documents listed below can be obtained from the EPA by:

- Calling (202) 564-9554,
- Sending an e-mail request to TRIDOCS@epa.gov, or
- Visiting the TRI Home Page (http://www.epa.gov/tri) or the TRI Guidance Documents Page (http://www.epa.gov/tri/guide_docs/index.htm.

I. General Guidance:

- **40 CFR 372, Toxic Chemical Release Reporting: Community Right-to-Know**
- **EPCRA Section 313 Questions and Answers-Revised 1998 Version** December 1998 (EPA 745-B-98-012)
- **EPCRA Section 313 Releases and Other Waste Management Reporting Requirements,** February 2001 (EPA 260/K-01-001)
- **Toxic Chemical Release Inventory Reporting Forms and Instructions Revised 2002 Version,** March 2003[4]

[4] The EPA publishes annually updates of reporting forms and instructional guidelines. You should review EPA's TRI web site for these updates and other updates pertaining to EPCRA reporting requirements. The TRI home page can be found at http://www.epa.gov/tri or the TRI Guidance Documents Page http://www.epa.gov/tri/guide_docs/index.htm.

II. Chemical-Specific Guidance

- **Emergency Planning and Community Right-to-Know Act-Section 313: Guidance for Reporting Releases and Other Waste Management Activities of Toxic Chemicals: Lead and Lead Compounds,** November 2001 (EPA-260-B-01-027)

- **Mercury guidance document**

III. Industry-Specific Guidance

- **EPCRA Section 313: Guidance for Chemical Distribution Facilities,**
  January 1999 (EPA 745-B-99-005)

- **Emergency Planning and Community Right-to-Know Act Section 313 reporting Guidance for the Presswood and Laminated Products Industry**,
  August 2001 (EPA 260-B-01-013)

- **EPCRA Section 313 Reporting Guidance for Rubber and Plastics Manufacturing,**
  May 2000 (EPA 745-B-00-017)

- **EPCRA section 313 Reporting Guidance for Spray Application and Electro deposition of Organic Coatings,**
  December 1998 (EPA 745-R-98-014)

Tanks – Filling and Storage

Pure MDI is a solid at room temperature and even though MDI/PMDI is a liquid at room temperature, both have a very low vapor pressure. There will be minor to almost negligible releases occurring during filling or storage due to changes in temperature from day to night.

Working Losses:

Working losses occur when MDI/PMDI vapor that is present over the liquid in a storage tank is displaced from the tank by the addition of MDI/PMDI liquid during tank filling. A reasonable worst-case estimate of working losses can be made based on the size and number of storage tanks, the average storage temperature, and the number of times each tank is filled in one year.

The calculations that follow demonstrate that working losses of MDI/PMDI will be very low under most normal storage circumstances

The working losses can be estimated from the following expression:

$$\mathbf{L_W = Q_W * (1 / 359) * (273.15 / T_{amb}) * (VP_{amb} / 760) * M_W * K_{mdi}}$$

Where:

L_W = the working losses in lb/year.

Q_W = the annual throughput of MDI pumped to the tank in ft^3/year.

T_{amb} = the storage temperature in °K.

VP_{amb} = the vapor pressure of MDI at the storage temperature in mm Hg
M_w = the molecular weight of MDI (250.26)
K_{mdi} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the storage temperature.

Example 1: Working Losses:

A facility receives 1,000,000 gallons of MDI/PMDI annually. Material is stored in a 20,000-gallon storage tank at an average temperature of 77°F (298.2 °K). Calculate the working losses for the year.

The working losses can be estimated from the following expression:

$$\mathbf{L_w = Q_w * (1 / 359) * (273.15 / T_{amb}) * (VP_{amb} / 760) * M_w * K_{mdi}}$$

Where:

L_w = the working losses in lb/year
Q_w = the annual throughput of MDI pumped to the tank in ft^3/year
T_{amb} = the temperature of the stored material
VP_{amb} = the vapor pressure of MDI at the storage temperature in mm Hg
M_w = the molecular weight of MDI (250.26).
K_{mdi} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the storage temperature

Q_w = 1,000,000 gallons/year. X 1 cu. ft./7.48 gal
Q_w = 133,690 cu. Ft.
T_{amb} = 298.2 °K.
Vp_{amb} = 1.0×10^{-5} mm Hg @ 298.2 °K
M_w = the molecular weight of MDI (250.26).
K_{mdi} = 0.55 for a 50/50 mixture of MDI/PMDI at 298.2 °K.
(See Appendix B: Table II: MDI/PMDI Adjustment Factors)

Therefore:

L_w = (133,690 cu. ft.)(1/359)(273.15/298.2)(1.0 10^{-5}/760)(250.26)(.55)
$\mathbf{L_w = 6.28 \times 10^{-4}}$ **lbs./yr.**

Breathing Losses:

Breathing losses occur because differences in temperature (such as changes between day and night temperatures) affect the vapor space pressure inside storage tanks. Vapors expand with an increase in temperature and contract with a decrease in temperature. In addition, the saturated vapor concentration of a substance in air increases with increasing temperature and decreases with a decreasing temperature. As outside temperature rises during the day, pressure inside a tank increases and air will be expelled from the tank. As the temperature falls during the night, pressure in the tank decreases and fresh airflows into the tank. MDI/PMDI mixtures are typically stored in temperature-controlled tanks, therefore losses for temperature controlled, refrigerated, or insulated tanks are assumed to be negligible.

The method used to calculate the breathing losses is an adaptation of an EPA method published in AP-42 (See Appendix C for development of formula). This modified method can only be used for materials that display very low vapor pressure characteristics.

The breathing losses can be determine using the following equations:

$$\mathbf{L_b = 365 * M_{air} * (VP_{amb} / 760) * M_w * K_{mdi}}$$

$$\mathbf{M_{air} = (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb})}$$

$$\mathbf{V_v = V_T * (100\text{-}L_T)/100}$$

$$\mathbf{K_E = T_R / T_{amb}}$$

Where:

L_b	=	the breathing losses in lb/year.
M_{air}	=	the total air displaced per day in lb-mole/day.
VP_{amb}	=	the vapor pressure of MDI at the ambient temperature in mm Hg
M_w	=	the molecular weight of MDI (250.26).
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
T_{amb}	=	the average ambient temperature in °K.
T_R	=	the average day-night temperature fluctuation in °K.
K_E	=	the vapor expansion factor due to day-night temperature fluctuation.

Example 2: Breathing Losses

A fixed roof vertical tank contains MDI/PMDI. The tank has a volume of 12,000 gallons (10' D x 20' H) and is maintained at an average daily capacity of 50%. The tank is located in New York area. From meteorological data, the daily average ambient temperature is 54.55 ^{o}F (12.53 ^{o}C) and the daily average temperature range is 15.3 ^{o}F (8.5 ^{o}C). The MDI/PMDI vapor pressure at the daily average temperature is 1.945×10^{-6} mm Hg.

The breathing losses can be calculated from the following expression:

$$\mathbf{L_b = 365 * M_{air} * (VP_{amb} / 760) * M_w * K_{mdi}}$$

$$\mathbf{M_{air} = (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb})}$$

$$\mathbf{V_v = V_T * (100\text{-}L_T)}$$

$$\mathbf{K_E = T_R / T_{amb}}$$

Where:

L_b	=	the breathing losses in lb/year.
M_{air}	=	the total air displaced per day in lb-mole/day.
VP_{amb}	=	the vapor pressure of MDI at the ambient temperature in mm Hg
M_w	=	the molecular weight of MDI (250.26)
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

T_{amb} = the average ambient temperature in °K.
T_R = the average day-night temperature fluctuation in °K.
K_E = the vapor expansion factor due to day-night temperature fluctuation.

V_v = $V_T * (100-L_T)$ = 12,000(100-50)/100 = 6,000 gallons
K_E = T_R / T_{amb} = $(8.5^o)/(12.53+273.15)$ = 0.02975

The total air displaced per day (M_{air} in lb-mole/day) is calculated from the following expression:

$$M_{air} = (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb})$$

M_{air} = (6,000/7.48) * (1/359) * (0.02975) * (273.15/285.68)
M_{air} = 0.0636 lb mole/day

The breathing losses can now be estimated from the following expression:

$$L_b = 365 * M_{air} * (VP_{amb} / 760) * M_w * K_{mdi}$$

L_b = $365 * (0. 0636) * (1.945 \times 10^{-6} /760) * (250.26) * (.54)$

L_b = 8.16×10^{-6} lbs/yr.

Fugitive Emissions (Non-point Source):

Fugitive emissions are air releases of volatile chemicals that typically occur due to leaks from fittings and seals in chemical process equipment, transfer operations or storage systems. Direct measurement or monitoring data can be used to estimate fugitive emissions. In the absence of direct measurement or monitoring data, industrial hygiene data on MDI concentrations in the workplace can be used to estimate MDI or MDI/PMDI fugitive emissions. ***This technique can only be used if the industrial hygiene data are representative of average concentrations throughout the year and throughout the building.***

The fugitive emissions can be estimated from the following expression:

$$\mathbf{L_{fg} = C_{mdi} * (V_B / 359) * N_{year} * (273.15 / T_{amb}) * M_w * K_f}$$

Where:

L_{fg} = the fugitive emissions in lb/year.
C_{mdi} = the average MDI concentration, in ppmv, in the air within the building.
V_B = the volume of the workspace building in ft^3.
N_{year} = the number of air exchanges per year.
T_{amb} = the ambient temperature in °K.
M_w = the molecular weight of MDI (250.26).
K_{fg} = the adjustment factor to the MDI concentration in the building air. API uses a value of 1.10

Example 3: Fugitive Emissions

The average concentration of MDI throughout the year was measured at 0.001 ppm for a process area that measured 50 ft W x 100 ft L and 20 ft in height. There are an average of 5 air changes per hour and the plant operates 16 hours/day, 250 days/year. The average temperature of the facility is 77^0F. Calculate the fugitive emissions.

The fugitive emissions can be estimated from the following expression:

$$\mathbf{L_{fg} = C_{mdi} * (V_B / 359) * N_{year} * (273.15 / T_{amb}) * M_w * K_f}$$

L_{fg} = the fugitive emissions in lb/year.
C_{mdi} = the average MDI concentration, in ppmv, in the air within the building.
V_B = the volume of the workspace building in ft^3.
N_{year} = the number of air exchanges per year.
T_{amb} = the ambient temperature in °K.
M_w = the molecular weight of MDI (250.26).
K_{fg} = the adjustment factor to the MDI concentration in the building air. API uses a value of 1.10

Calculating:

C_{mdi} = 0.001ppm = 1.0×10^{-9}
V_B = (50 ft x 100 ft x 20 ft) = 100,000 ft^3
N_{year} = the number of air exchanges per year.
N_{year} = (5 changes/hr x 16 hr/day x 250 days/yr) = 20,000 changes/year
T_{amb} = 298.2 °K.
M_w = the molecular weight of MDI (250.26).
K_{fg} = the adjustment factor to the MDI concentration in the building air. API uses a value of 1.10

Therefore:

$$L_{fg} = (1.0 \times 10^{-9}) * (100{,}000\ ft^3/359) * (20{,}000) * (273.15/298.2) * (250.26) * (1.1)$$

$$\mathbf{L_{fg} = 1.43\ lbs/year.}$$

Equipment Leaks

In cases where monitoring data are not available, EPA has developed a method using emission factors based upon the type of fittings and number of fittings used in the process. The methodology used for MDI/PMDI is an adaptation of an EPA Correlation Method ("1995 Protocol for Equipment Leak Emission Estimate" - EPA-453/R-95-017). The method presented here uses the actual formulas recommended by the EPA except that saturated vapor concentrations are used instead of screening values. Since the vapor concentration of MDI cannot exceed the saturation vapor pressure at a given temperature, the predicted screening values are limiting and conservative values. The calculation methodology involves the following steps:

1. Determine the saturated concentration of MDI.
2. Calculate emission factor for each equipment type.

3. Determine emissions for each equipment type.
4. Determine total losses from equipment leaks.

The MDI emissions from equipment leaks using the Modified Correlation Approach can be determined using the following equations:

$$SV = [1{,}315.8 \times 10^{[(10.902 - 4634.09/(266.15 + t)]}]$$

Where:

SV = Screening Value in ppmv and
t = Temperature in ^{o}C.

The calculated Screening Value (SV) is then inserted into the Leak Rate/Screening Value Correlation Formula for the appropriate equipment type (found in Table V-6) and the leakage rate is determined.

Table V-6
Leak Rate/Screening Value Correlations

Equipment Type	Correlation Leak Rate (kg/hr) ($a*(SV)^b$)
Gas Valve	$1.87 \times 10^{-06} \times (SV)^{0.873}$
Light Liquid Valve	$6.41 \times 10^{-06} \times (SV)^{0.787}$
Light Liquid Pump [c]	$1.90 \times 10^{-05} \times (SV)^{0.824}$
Connectors	$3.05 \times 10^{-06} \times (SV)^{0.885}$

c This equation can be used for liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pumps.

The total emissions from equipment leaks will be equal to the emissions contributed from each gas valves, light liquid valves, light liquid pumps, and connectors.

For gas valves:

$$K_{gas} = 1.87 \times 10^{-6} * (C_{mdi})^{0.873}$$

For liquid valves:

$$K_{liq} = 6.41 \times 10^{-6} * (C_{mdi})^{0.787}$$

For liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pumps:

$$K_{pump} = 1.90 \times 10^{-5} * (C_{mdi})^{0.824}$$

For connectors:

$$K_{con} = 3.05 \times 10^{-6} * (C_{mdi})^{0.885}$$

Where:

K_{gas} = the emission factor for gas valves in kg/year-item.
K_{liq} = the emission factor for liquid valves in kg/year-item.

K_{pump} = the emission factor for liquid pumps in kg/year-item.
K_{con} = the emission factor for connectors in kg/year-item.

For Gas Valves the emissions can then be estimated from the following expression:

$$\mathbf{L_{gv} = K_{gas} * n_{gv} * K_{mdi} * t_{pr}}$$

L_{gv} = the annual losses from liquid valves in lb/yr.
n_{gv} = the number of liquid valves.
K_{mdi} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
pr = the total time in hours/year that the process is operating.

For Liquid Valves the emissions can then be estimated from the following expression:

$$\mathbf{L_{liq} = K_{liq} * n_{liq} * K_{mdi} * t_{pr}}$$

L_{liq} = the annual losses from liquid valves in lb/yr.
n_{liq} = the number of liquid valves.
K_{mdi} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
t_{pr} = the total time in hours/year that the process is **operating**

For liquid Pumps the emissions can then be estimated from the following expression:

$$\mathbf{L_{pump} = K_{pump} * n_{pump} * K_{mdi} * t_{pr}}$$

L_{pump} = the annual losses from liquid valves in lb/yr.
N_{pump} = the number of liquid valves.
K_{mdi} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
t_{pr} = the total time in hours/year that the process is operating

For Connectors the emissions can then be estimated from the following expression:

$$\mathbf{L_{con} = K_{con} * n_{con} * K_{mdi} * t_{pr}}$$

L_{con} = the annual losses from liquid valves in lb/yr.
n_{con} = the number of liquid valves.
K_{mdi} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
t_{pr} = the total time in hours/year that the process is operating

Total Emissions can then be estimated from the following expression:

$$\mathbf{E_{tot} = L_{gas} * L_{liq} * L_{pump} * L_{con}}$$

Table V-7: Equipment Leak Emission factors (lb./hr-component) @ 50 ^{o}C represents the emissions factors associated with each fitting in service at a temperature of 50 ^{o}C. If you know the number of fittings, multiply the emission factor by the number of fittings and add the total up to get the annual emissions from equipment leaks.

Table V-7
Equipment leak Emission Factors lbs/hr-component @ 50 ^{o}C

Equipment Type	Temp. ^{O}C	Vapor Pressure (mm Hg)[4]	Screening Value (SV)[5] (ppmv)[2]	Equation Constant (a)	Equation Constant (b)	Emission Factor[1] (kg/hr)[3]	Emission Factor[1] (lb./hr)[3]
Gas Valves	50	$1.80x10^{-04}$	$2.37x10^{-01}$	$1.87x10^{-06}$	0.873	$5.33x10^{-07}$	$1.18x10^{-06}$
Light Liquid Valves	50	$1.80x10^{-04}$	$2.37x10^{-01}$	$6.41x10^{-06}$	0.797	$2.04x10^{-06}$	$4.49x10^{-06}$
Light Liquid Pumps	50	$1.80x10^{-04}$	$2.37x10^{-01}$	$1.90x10^{-05}$	0.824	$5.81x10^{-06}$	$1.28x10^{-05}$
Connectors	50	$1.80x10^{-04}$	$2.37x10^{-01}$	$3.05x10^{-06}$	0.885	$8.54x10^{-07}$	$1.88x10^{-06}$

Illustrative example 1: Estimate MDI emissions from equipment leaks in a MDI manufacturing facility with the following equipment type counts:

(1) 3000 valves in light liquid service
(2) 4500 connectors.
(3) 20 pump seals
(4) 2 agitators

The MDI concentration in the stream is 12.7% and the air temperature is 50 ^{o}C.

The total emissions due to equipment leaks using the Modified Correlation Emission Factors are found in Table V-8.

TableV-8
Equipment Leak Emissions Modified Correlation Screening Factors

Equipment Type	Service	Number Components	Weight Fraction	Modified Corr. Factors	Emissions (lbs/hr)	Emissions (lbs./year)
Valves	Light Liquid	3000	0.127	$4.49x10^{-06}$	$1.71x10^{-03}$	15
Pumps	Light Liquid	20	0.127	$1.28x10^{-05}$	$3.25x10^{-05}$	0.285
Agitators	Light Liquid	2	0.127	$1.28x10^{-05}$	$3.25x10^{-06}$	0.0285
Connectors	All	4500	0.127	$1.88x10^{-06}$	$1.07x10^{-03}$	9.41
					Total	24.7

Spills:

Section 313 of the Emergency Planning and Community Right-to-Know Act requires that you account for material lost because the chemical was spilled onto the ground, resulting in an air release. Evaporative releases from spills depend upon many factors including

1. The volatility of the material
2. The size of the spill
3. The temperature of the surrounding area

4. The wind speed
5. The time that the liquid from the spill is allowed to evaporate

A fairly simple model proposed by the EPA that accounts for all these factors is provided by the following equation:

$$\mathbf{Q_R = (0.003413) * (u)^{0.78} * A_{spill} * (VP_{MDI}/T_{spill}) * (MW)^{\wedge 2/3} * K_{MDI}}$$

Where:

Q_R	=	the evaporation rate in lb/min.
u	=	the airflow in m/sec. This is the airflow in the vicinity of the process.
A_{spill}	=	the area of the spilled material in ft^2..
VP_{MDI}	=	the vapor pressure of MDI in mm Hg. at the filling temperature
T_{spill}	=	the average evaporation temperature in °K.
MW	=	the molecular weight of MDI (250.26).
K_{MDI}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The spill losses can be determined by multiplying the evaporation rate (QR) in lb/min by the time the spill is on the ground and converting the calculated value to the desired units:

$$\mathbf{L_{spill} = QR * t_{spill} * (60)}$$

Where:

L_{spill}	=	the evaporation losses resulting from the spill in lb.
QR	=	the evaporation rate in lb/min.
t_{spill}	=	the time that the spill is on the ground in hours.

A facility while transferring a 50% mixture of MDI/PMDI from the storage tank to the day tank develops a leak at a flange that results in a spill of 75 gallons of material. A liquid pool that has a surface area of 200 ft^2, remains on the floor for eight hours before a HAZMAT Team could be assembled. During that time, the wind speed remained at a constant 20 miles/hour (9 m/s). The temperature of the process area was a constant 70 ^oF (298.4 ^oK). Determine loss of material caused by evaporation.

Air emissions released because of the spill of MDI/PMDI can be calculated using EPA's proposed model:

$$\mathbf{Q_R = (0.003413) * (u)^{0.78} * A_{spill} * (VP_{MDI}/T_{spill}) * (MW)^{\wedge 2/3} * K_{MDI}}$$

Where:

Q_R	=	the evaporation rate in lb/min.
u	=	the airflow speed in m/sec. This is the airflow in the vicinity of the process
A_{spill}	=	the area of the spilled material in ft^2.
VP_{MDI}	=	the vapor pressure of MDI in mm Hg. at the filling temperature
T_{spill}	=	the average evaporation temperature in °K.
MW	=	the molecular weight of MDI (250.26).
K_{MDI}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

Therefore:

Q_R	=	lb./minute
u	=	9.0 m/sec.
A_{spill}	=	200 ft^2.
VP_{MDI}	=	6.1 x 10^{-6} mm Hg
T_{spill}	=	298.4°K.
MW	=	250.26
K_{MDI}	=	0.54

Substituting the appropriate values into the equation, the emissions released due to the spill is equal to:

$$\mathbf{Q_R = (0.003413) * (9.0)^{0.78} * 200 * (6.1 \times 10^{-6}/298.4) * (250.26)^{\wedge 2/3} * (0.54)}$$

$$\mathbf{Q_R = 2.90 \times 10^{-6} \text{ lbs./min}}$$

Using the equation:

$$\mathbf{L_{spill} = QR * t_{spill} * (60)}$$

Where:

L_{spill} = the evaporation losses resulting from the spill in lb.
QR = the evaporation rate in lb/min.
t_{spill} = the time that the spill is on the ground in hours

The total amount of MDI/PMDI from the spill is:

$$L_{spill} = (\mathbf{Q_R = 2.90 \times 10^{-6} \text{ lbs./min})* (8 \text{ hours}) * (60 \text{ min/hr.})}$$

$$\mathbf{L_{spill} = 1.40 \times 10^{-3} \text{ lbs.}}$$

Disposal and Treatment:

Activities that involve the disposal and/or treatment of an EPCRA Section 313 chemical on-site or off-site must be reported. These activities are (but are not limited to):

- Discharges to surface waters
- Releases to land
- Releases to injection wells
- Surface impoundment
- On-site waste treatment, energy recovery, recycling
- Discharges to POTW
- Off-site waste disposal
- Transfer for energy recovery

Discharges to receiving streams or water bodies are usually accountable in the facilities NPDES permit. The permit lists the reported chemicals with limits on the quantity that can be discharged. Regulations require testing for amount of chemicals being discharged. You must also report releases contributed to storm water run-off.

On-site releases to land are accountable under histories and spill records, which are required under Section 304 of EPCRA and Section 112 (r)(7)(B)(ii) of the Clean Air Act. EPCRA chemicals sent to off-site RCRA landfills must

be reported. Hazardous waste manifests contain description of waste and list waste composition that will aid you in calculating amount of Section 313 chemical being disposed.

Facilities that use surface impoundment, as a disposal method should keep records of waste stream composition. This can be used in determining the percentage of volatile chemicals that will be evaporated. This release determination will be reported under fugitive emissions.

Releases of EPCRA 313 chemicals that are discharged into publicly owned treatment works POTWs must be reported. If totals are less than a 1,000 pounds you may report that amount using a range, but if the quantity exceeds 1,000 pounds than you must report the exact estimate. Bases for determining the amount of EPCRA 313 chemical discharged is usually based upon stream analyses and monitoring data that is required by permit.

Transfers to off-site locations for the purposes of disposal, treatment, energy recovery or recycling must be reported. Estimates of quantities for these purposes are based upon chemical content contained in the overall waste. Materials that are shipped off-site for these purposes must be manifested. The manifest requires the listing of the chemical content. Analyses usually specify a range and judgment should be used in determining the amount. Transfers may also include any material that may include residuals in bags, totes, drums, tank trucks, and wasted product. Estimates of residual content can range from 0 to 3% depending upon viscosity of the material. MDI is a solid while a mixture of MDI/PMDI is a liquid at room temperature. If you properly decontaminate the containers, in accordance with recommended procedures, before disposal, the amount of MDI and MDI/PMDI can be considered negligible. However, if you decontaminate containers you must report this as treatment and the amount of material treated and its treatment efficiency must be reported.

The bases for determining all releases fall into one of four categories:

- Monitoring data and direct measurement
- Mass balance
- Emission factors derived from scientific studies and are chemical, equipment, through-put, and chemical specific
- Engineering calculations using published mathematical formulas or best engineering judgment

Judgment as to which method to use is critical. One has to weigh the validity of the data being presented along with the actual physical nature of the process and chemical to determine if the number calculated is correct. Over reporting has serious consequences as well as under reporting, so think and let sound judgment prevail when determining releases.

Stack Emissions (Point Source):

Stack emissions are releases of EPCRA Section 313 chemicals that are contained in confined air streams. Examples are emissions from stacks, vents, ducts, pipes and storage tanks. Emissions from pollution control equipment are also included in this category. In the following section we will be looking at various applications were MDI and MDI/PMDI mixture are being used. Stack emissions will be calculated using sound engineering judgment.

The applications were MDI and MDI/PMDI are used fall into the following three areas:

1. Enclosed Process (Cavity and Foam Density)
2. Open Process
3. Specialty Process

The enclosed process estimation can be used for applications where the MDI-based products are introduced into a mold or cavity by injection, poured, or sprayed and will expand to fill the space. The MDI based resin may remain in the cavity in a final product or it may be released as a molded article. Examples of applications that can be considered as enclosed processes are:

- Reaction Injection Molding (RIM)
- Molded foam parts (automotive, furniture)
- Cast elastomers (shoe soles, packaging, furniture)
- Pout-in-place (appliance insulation, marine products,)
- Sandwich panels

The basic assumption used in calculating MDI and MDI/PMDI releases from closed mold/cavity processes is that MDI or MDI/PMDI saturated air first fills the volume of the mold cavity during each use and is forced out into the environment as the chemicals are added.

The curing of an isocyanate-based product is almost accompanied by the generation of heat (exothermic reaction takes place). The concentration of MDI or MDI/PMDI in air depends on temperature. The higher the temperature the more material is volatilized and the saturated vapor concentration in air increases. Therefore, it is important to establish a maximum temperature at which the MDI or MDI/PMDI is likely to escape from a curing product. The relationship between vapor pressure and temperature is not linear but logarithmic; therefore the vapor pressure vs. temperature chart should be used to determine the correct vapor pressure for MDI or MDI/PMDI.

The open process estimation can be used for applications where the MDI-based products are introduced into a mold or cavity, but are cured with a significant fraction of the MDI containing product exposed to the atmosphere, or in which the MDI-base product is layered, sprayed or coated onto a surface. Examples of open process applications are:

- Slabstock/Bunstock
- Laminate boardstock
- Metal skin panels
- Carpet backing/flooring
- Bonded foam production
- Coatings
- Spray foaming
- Adhesives/sealants

The basic assumption used in calculating MDI and MDI/PMDI releases from open processes is that MDI and MDI/PMDI vapor will volatize from all exposed surfaces of a curing foam, adhesive, coating, or other MDI-containing product. Evaporative releases from open processes (or spills) depend upon many factors including:

1. The volatility of the material
2. The surface area from which evaporation occurs
3. The temperature of the curing product
4. The airflow, and
5. The duration of the activity

To illustrate both enclosed and open processes, the guidebook will address the following applications:

1. Adhesive
2. Air Filters
3. Appliance
4. Appliance Truck
5. Automotive
6. Belt & Cord
7. Boardstock (open process)
8. Boats
9. Doors
10. Filling/Blending

11. Foundry
12. Laminator (cavity)
13. Mobile Homes/Motor Homes
14. Oriented Strand Board (OSB)
15. Packaging
16. Rebond
17. Rug and Carpet
18. Spandex
19. Spray Foam -Motor Home Roof Caps
20. Spray Booth Emissions
21. Water Heaters

A worst-case scenario will be presented for each application. The stack emissions will be presented in a step-by-step solution. The section on losses generated from storage tanks and fugitive emissions should be consulted for step-by-step description for calculating these emissions.

Illustrated Process Stack Emissions Examples

1.0 Adhesives/Coatings

Mixtures of methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) used as an adhesive are applied using a number of various ways. They can be rolled, sprayed, brushed, or applied using special applicators. These adhesives come in both two-component and one-component systems, and can be either water-based or solvent based. Depending on the formulation, they are applied at room temperature or as a hot melt. These adhesives usually have a set time and an open time ranging from 30 seconds to 4 minutes and a "tack-free time of 5 to 30 seconds. Once applied, the adhesive is activated by air, heat, UV light, and/or by surface contact.

Process Description:

A 2 percent mixture of MDI is applied to both sides of a 4 ft. x 8 ft. wood panel using a special roller applicator system. Material, solid at room temperature, is pre-heated to 70^{o}F to allow material to flow from the drum to applicator rollers. The rollers are heated and maintained at 275^{o}F. Material is applied to both surfaces at a thickness of 1-2 mils and passed through an UV light. The wood paneling is placed over the wall and floor sections and pressure applied to the sheeting. Set up time is 30 seconds. Tack time is 5 seconds. A blower operating at 550 CFM is used to carry off any emissions during application of the adhesive. The length of the roller surface is 5 ft. x 1 ft. The adhesive is applied at a rate of 11.5 grams/ft^2. Process covers at a rate of 2,465 ft^2/hour. Plant operates 24 hours a day 365 days a year (8760 hours a year).

Calculating Stack Emissions:

MDI will migrate from all exposed surfaces and all losses will be the result from evaporation. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the "tack-free" time and the exposed surface area.

The calculation methodology involves the following steps:

1. Determine partial pressure of MDI at "tack-free" temperature.
2. Determine the exposed area.
3. Determine evaporation rate.

The evaporation rate (in grams/day) is determined from the following expression:

$$W = 25.4 * VP_{MDI} * (M_W / T_{proc}) * (u)^{0.78} * S_A * t_{TF}$$

Where:

W	=	the evaporation losses from the open process in gr./day.
VP_{MDI}	=	the vapor pressure of MDI in atmospheres @ process temperature.
T_{proc}	=	the process temperature in °K.
M_W	=	the molecular weight of MDI
u	=	the airflow speed in m/sec.
S_A	=	the exposed surface area in M^2.
t_{TF}	=	the "tack-free" time in seconds.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Step I: Determine Vapor Pressure of 2% MDI @ 275 ^{O}F in Atmospheres.

The vapor pressure of MDI @ 275 ^{O}F is 2.278 x 10 $^{-1}$ mm.
Converting this to atmospheres and for a 2% mixture of MDI.
The vapor pressure (VP_{MDI}) of 2% MDI @ 275 ^{O}F is:

$\boldsymbol{VP}_{MDI}$ = (2.278 x 10 $^{-1}$mm)(1 atm/760mm)x (2 lbs. MDI/ 100 lbs. Mixture)

$\boldsymbol{VP}_{\mathbf{MDI}}$ = **5.99 x 10^{-6} atmospheres**

Step II: Determine Ventilation Rate in Meters/Second.

Ventilation rate (u)	=	Velocity @ STP/Surface Area
Roller Surface Area	=	1 foot by 5 feet = 5 ft^2
Velocity @ STP	=	550 ACFM x 298^{O}K/308^{O}K
Velocity	=	532SCFM
Ventilation rate (u)	=	Velocity/Surface Area
	=	532SCFM/ 5ft^2 x min./60 sec x .3048 m/ft.
Ventilation rate (u)	**=**	**5.41 x 10^{-1} meters/second**.

Step III: Determine Tack Time.

The problem states that the tack-free time is 5 seconds.

Step IV: Determine the Exposed Surface Area.

The exposed surface area is determined from the area of panel board processed.
The roller applicator coats 2465 ft^2/hr.
Based upon 24 hour production:
Total Exposed Surface Area (S_A)/day:

S_A = 2465 ft^2 x 24 hours/day

S_A = 5.92 x 10^{+4} ft^2/day

Converting ft^2 to M^2:

S_A = 5.92 x 10^{+4} ft^2/day x M^2/10.76 Ft^2

$\mathbf{S_A}$ = **5.50 x 10^{+3} M^2 / day**

Therefore:

W = 25.4 * VP_{MDI} * (MW / T_{proc}) * (u)$^{0.78}$ * S_A * t_{TF}

= (25.4)(5.99x10^{-6})atm(250.26)/408)(5.41x10^{-1})$^{0.78}$ m/sec(5.50x10^{+3})ft^2(5)sec

W = **1.61 grams./ day**

Step V: Convert Grams per Day to Pounds per Year

W = 1.63 grams/day x 1 pound/454 grams x 365 days/year

W = **1.30 pounds / year**

2.0 Air Filters

A mixture of methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) is reacted with a polyol blend to make a gasket or to become part of an air filter housing. The polyol and the diisocyanate are brought together and reacted in a customized piece of equipment, which then dispenses the reacting mixture into a cavity. The cavity is then passed through a heated oven to cure the polyurethane formed by the diisocyanate/polyol reaction.

Process Description:

A polyurethane mixture with a ratio of 1.82 (polyol to MDI/PMDI) is dispersed into a mold cavity and then heated to 145^{o}F in an oven. The dispenser disperses through a customized nozzle head at a rate of 0.2579 lbs. Polyol/MDI/PMDI mixture per filter. The production lines producers 670 filters/hour. The diameter of the filter is 9 inches. Tack time is 2 seconds.

Calculating Stack Emissions:

To calculate the emissions for this process, the worst-case scenario will be presented. The MDI/PMDI emissions will be generated from two areas. Emissions are released as (1) component A and Component B mixture is being dispensed into the cavity and (2) as it is passed through the oven to be cured. Therefore, the total amount of MDI/PMDI emitted will equal the amount emitted while being dispersed plus the amount released during curing.

The total amount of emissions emitted during dispensing operations will correspond to the total volume of air displaced at the temperature of the process. A reasonable worst-case estimate of emissions can be made based upon the volume of the mold cavity, the number of pieces produced per year, and the maximum process temperature.

The enclosed process losses can be estimated from the following expression:

$$\mathbf{L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}}$$

Where:

L_c	=	emissions from the enclosed process in lb./year.
V_{air}	=	the annual volume of displaced air in ft^3/year.
T_{proc}	=	the temperature material is dispensed at in °K.
VP_{MDI}	=	the vapor pressure of MDI in mm Hg. at dispensed temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0^{o}C and 1-atmosphere.

Step I: <u>Determine Annual Volume Displaced (V_{air})</u>

V_{air}	=	N_f * M_{disp} * ρ *
V_{air}	=	Annual Volume in Ft^3/yr.
N_f	=	Annual Number of Filters Processed
M_{disp}	=	Amount of Material Dispensed/Filter
ρ	=	Density of Material lbs./ft^3

Therefore:

V_{air} = (670 filters/hr.)(8760 hr./yr.)(0.26 lbs./filter)(1 gal/10lbs)1 ft^3/7.48gal)

V_{air} = $2.04 \times 10^{+4}$ ft^3/year

Step II: <u>Convert Dispenser Temperature to ^oK</u>

T_{proc} ^oK = (273 ^{o} + ^{o}C)

T_{proc} ^oK = (273^o + 62.8 ^{o}C)

T_{proc} ^oK = 335.8

Step III: <u>Determine the Vapor Pressure of MDI @ 335.8 ^oK</u>

The vapor pressure of MDI @ 335.8^{o}K from chart is 6.663×10^{-4} mm

Step IV: <u>Determine Adjustment Factor</u>

The adjustment factor can be determined knowing that the ratio of polyol to MDI/PMDI mixture is 1.89.

Therefore:

% MDI/PMDI = (1 / ratio + 1)(100)

= (1/1.89 + 1)100

% MDI/PMDI = 34.6

From Chart:

K_{MDI} = 0.47

Therefore:

Losses due to cavity fill is:

L_C = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI}/ 760) * M_w * K_{MDI}

= V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI}/ 760) * M_w * K_{MDI}

= ($2.04 \times 10^{+4}$ ft^3/year)(1/ 359)(273.15/335.8)(6.663×10^{-4} mm / 760) (254.38)(0.47)

L_C = 4.85×10^{-3} lbs./year

Losses During the Curing Phase:

For this situation it is assumed that MDI will migrate from all exposed surfaces and all losses will be the result from evaporation. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the "tack-free" time and the exposed surface area.

The calculation methodology involves the following steps:

1. Determine partial pressure of MDI at "tack-free" temperature.
2. Determine the exposed area.
3. Determine evaporation rate.

The evaporation rate (in grams/day) is determined from the following expression:

$$\mathbf{W = 25.4 * VP_{MDI} * (M_W / T_{proc}) * (u)^{0.78} * S_A * t_{TF}}$$

Where:

W	=	the evaporation losses from the open process in gr./day.
VP_{MDI}	=	the vapor pressure of MDI in atmospheres @ process temperature.
T_{proc}	=	the process temperature in °K.
M_W	=	the molecular weight of MDI
u	=	the airflow speed in m/sec.
S_A	=	the exposed surface area in M^2.
t_{TF}	=	the "tack-free" time in seconds.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Step I: Determine Vapor Pressure of MDI @ 145 ^{o}F in Atmospheres.

The vapor pressure of MDI @ 145 ^{o}F is 6.682 X 10 $^{-4}$ mm.
Converting this to atmospheres:

The vapor pressure (VP_{MDI}) MDI @ 145 ^{o}F is :

VP_{MDI} = (6.682 x 10 $^{-4}$mm)(1 atm/760mm)

VP_{MDI} = 8.792 x 10^{-7} atmospheres

Step II: Determine Ventilation Rate in Meters/Second.

Ventilation rate (u)	=	Velocity @ STP/Surface Area
Ventilation Area	=	4 ft. x 3 ft. = 12 ft^2
Velocity @ STP	=	990 acfm x 298^{o}K/336^{o}K
Velocity	=	878 scfm
Ventilation rate (u)	=	Velocity/Surface Area
	=	878 scfm/ 12ft^2 x min./60 sec x .3048 m/ft.
Ventilation rate (u)	**=**	**3.72 x 10^{-1} meters/second.**

Step III: <u>Determine Tack Time.</u>

The problem states that the tack-free time is 2 seconds.

Step IV: <u>Determine the Exposed Surface Area.</u>

The exposed surface area is determined from the area of exposed filter. Since the filter is conical in shape only the top surface is exposed.

Exposed Surface Area = $\Pi r^2 = \Pi(4.5/12)^2 = 0.44$ ft^2
Based upon 24 hour production:

Total Exposed Surface Area (S_A)/day = 0.44 ft^2 /filter x 670 filters/hr. x24 hours/day

S_A = 7.08 x 10^{+3} ft^2/day x 1m^2/10.77 ft^2

S_A = 658 m^2

Therefore:

$$\mathbf{W = 25.4 * VP_{MDI} * (M_w / T_{proc}) * (u)^{0.78} * S_A * t_{TF}}$$

$$W = (25.4)(8.8\text{x}10^{-7})\text{ATM}(250.26/335.8)(3.72\text{x}10^{-1})^{0.78}\ \text{m/sec}(658\ )\text{m}^2(2)\text{sec}$$

W = 0.0103 grams MDI/day

We must multiply this by the KMDI correction factor to get pounds of MDI/PMDI emitted
KMDI is 0.47. Therefore,

W = 0.00485 grams MDI/day

Step V: <u>Convert Grams per Day to Pounds per Year</u>

W = 0.00485 grams/day x 1 pound/454 grams x 365 days/year

W = 0.004 pounds / year

<u>Total Emissions:</u>

$T_T = L_C + W$

T_T = 4.85 x 10^{-3} lbs./yr. + 4.0 x 10^{-3} lbs./yr.

T_T = 8.85 x 10^{-3} lbs./yr.

3.0 Appliances

Methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol resin blend to provide insulation inside the appliance frame. The two-component system will be injected through a spray nozzle inside the appliance frame after the appliance has been assembled and allow the polyurethane to expand filling the closed cavity. The two-component system will also be injected into the cavity after the inner backing has been installed and a plate placed over outer backing allowing the polyurethane to expand

to the contour of the framing while being passed through a curing stage. After the polyurethane has cured, the appliance is assembled and the excess foam is removed.

Process:

The manufacturing process consists of four assembly lines that can be modified to accommodate different appliances. The system handles the manufacture of washers, dryers, refrigerators, and freezers. All processes are closed systems that use a two-component system where MDI and polyol resin are fed from day tanks and are mixed together in a specially designed spray head and the material is injected into the door frame and/or of the side frames. The process is set up where all the equipment are isolated and contained in enclosed areas with separate exhaust systems.

Application I:

Door cavity is injected with MDI/polyol resin mix. Cover is placed over door cavity to form sealed compartment. System is then moved down conveyor. When doorframe gets to end of conveyor, system top plate is removed and excess foam is scrapped off.

Application II:

Carousel System allows for the injection of MDI/polyol resin mixture into the door housing. The door housing is placed into a chamber with a self-contained exhaust system. Exhaust system is located on roof. Plate is placed over door housing and given cure time. System rotates in a carousel like fashion (less space needed compared to conveyor system). Plate is removed and door removed from system.

Application III:

System consists of spray chamber where MDI/polyol resin mixture is injected into appliance frame cavity. Plate is placed over frame and moved down conveyor system. At end of conveyor system plate is removed and excess material removed before frame is place on assembly line.

Application IV:

The process system, consisting of three chambers, is injected at the same time. System operates from one to three chambers depending upon product being run and number of units required.

The facility runs all four lines 24 hours a day 365 days a year. Line A and B produces at a rate of 100 doors per hour consuming an average of 123 lbs. MDI per hour. Line C producers 150 frames an hour consuming 12,226 lbs. MDI per hour. Line D producers 100 frames an hour consuming 1,343 lbs. MDI per hour. The annual amount of MDI consumed for each line is 1.08, 10.74, and 11.778 million pounds respectively. The process is run at 85^{o}F. The size of the cavity changes but the density remains at 2.0 lbs/ft^3

Calculating Stack Emissions

To estimate emissions from closed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the “tack free” or “string” time during the curing process.

The enclosed process losses can be estimated from the following expression since the temperature of each line is the

same:

$$\mathbf{L_{fd} = VT_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}}$$

Where:

L_{fd}	=	emissions lb./year.
VT_{air}	=	total annual volume of displaced air in ft^3/year by all lines.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0^oC and 1-atmosphere.

Step I: <u>Calculate Annual Volume of Displaced Air (V_{air}) for each Line</u>

V_{air} = (Annual consumption of Polyol/MDI/PMDI)/ (Foam Density)

Line 1: V_{air} = 1.08 $x10^6$ lbs/year / 2.0 lbs/cu. ft. = 5.4 $x10^5$lbs/year

Line 2: V_{air} = 1.08 $x10^6$ lbs/year / 2.0 lbs/cu. ft. = 5.4 $x10^5$lbs/year

Line 3: V_{air} = 10.74 $x10^6$ lbs/year / 2.0 lbs/cu. ft. = 5.37 x 10^6 lbs/year

Line 4: V_{air} = 11.78 $x10^6$ lbs/year / 2.0 lbs/cu. ft. = 5.89 x 10^6 lbs/year

Total volume displaced equals:

V_{tair}	=	Line 1 + Line 2 + Line 3 + Line 4
V_{tair}	**=**	**123.4 x 10^5 ft^3/year**

Step II: <u>Determine vapor pressure of MDI @ 85^oF</u>

The vapor pressure of MDI @ 85 ^oF is 1.733 x 10^{-5} mm Hg

Step III: <u>Determine Temperature of Process in ^oK</u>

Converting 85 ^oF to ^oK:

^oK	=	(^oF-32)5/9+ 273.15
^oK	**=**	**302.6**

Step IV: <u>Determine Adjustment Factor K_{MDI}</u>

K_{MDI} = 0.56 @ 302.6 ^oK

Therefore:

L_{fd} = VT_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w* K_{MDI}

L_{fd} = (1.234 x 10^{7} ft^3/year) (1/359) (273.15/302.6) (1.733 x 10^{-5} mm Hg/760) (250.26) (0.56)

L_{fd} = 0.10 lbs/year

4.0 Appliance – Truck

Methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture (Part A) is used in conjunction with a polyol blend (Part B) in the manufacture of truck trailers insulation. This mixture is injected into the cavity walls to form the insulation barrier between the inner and outer wall. The two parts are mixed in a customized system that mixes within the dispenser head and material dispersed into a cavity. The foam adheres to the wall cavity**.**

Process Description:

A two-component system, (consisting of a polyol to MDI/PMDI ratio of 93lbs. to 100 lbs.) is injected into the walls, floors, ceilings, and doors of tractor-trailer bodies to form insulation. The material is injected at a temperature of 78 ^{o}F. Amounts of material required for trailers of various lengths is as follows:

Trailer length	Amount of material required
28 ft.	565 lbs.
36 ft.	801 lbs.
45 ft.	802 lbs.
51 ft.	1,000 lbs.

The foam density is 2.25 lbs./ft^3. The annual consumption of material used was 10.5 million pounds. The percent of MDI in component A is 52. The trailer to be injected is placed inside a containment area that has an individual exhaust system.

Calculating Stack Emissions

To estimate emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the “tack free” or “string” time during the curing process.

The enclosed process losses can be estimated from the following expression:

L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}

Where:

L_{fd} = emissions lb./year.

V_{air} = annual volume of displaced air in ft^3/year.

T_{proc} = process temperature in °K. (maximum temperature of the MDI).

VP_{MDI} = vapor pressure of MDI in mm Hg. at process temperature.

M_w = 250.26 (this is the molecular weight of MDI).

K_{MDI} = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0^oC and 1-atmosphere.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

V_{air} = (Amount of material processed/year)/Foam Density

V_{air} = $(1.05 \times 10^{+7}$ lbs./year)(1/2.25 lbs./ft^3

V_{air} = $4.67 \times 10^{+6}$ ft^3/yr.

Step II: Calculate Process Temperature in ^oK

The process temperature is 78 ^oF or;

T_{proc} = 298.7 ^oK

Step III: Determine vapor Pressure of MDI @ 298.7 ^oK (VP_{MDI})

The vapor pressure @ 298.7 ^oK is 1.072×10^{-5}mm

Step IV: Determine Adjustment factor (K_{MDI})

To determine adjustment factor (K_{MDI}), the percent of MDI in the blend must be determined. The ratio of Polyol to MDI/PMDI is 93/100. Therefore, the percentage of MDI/PMDI is:

%MDI/PMDI = (100/(100 + 93)) * 100

%MDI/PMDI = 51.8 %

The percent MDI in the MDI/PMDI mixture is 52%. Therefore the percent MDI in the blend is equal to

%MDI = (51.8) * (52.0)

%MDI = 26.9

Adjustment factor @ 298.7 ^oK and 26.9% MDI is 0.35

Therefore:

$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$

L_{fd} = $(4.67 \times 10^{+6} ft^3/yr.)(1/359)(273.15^oK / 298.7^oK)(1.072 \times 10^{-5}$ mm/760)(250.26)(0.35)

L_{fd} = 0.015 lbs. / year.

5.0 Automotive

Releases of MDI/PMDI will be calculated for an automotive assembly facility that produces a variety of interior and exterior parts with MDI-based rigid foam. The facility uses a total of 1,500,000 pounds of feedstock that includes an MDI/PMDI-containing component and a polyol/catalyst/blowing agent component. The MDI/PMDI component is purchased in bulk and stored indoors in a 6,000-gallon tank. The storage tank is filled 25 times each year. MDI is transferred to a 1,500 lb. day tank as needed. The day tank is stored indoors. The MDI is pumped directly from the day tank to the foam mixer head. It may be difficult to estimate the cavity size of each part that is filled with the system. MDI releases can instead be estimated from the target foam density for the automotive part and the total quantity of foam feedstock that is used in the year. The average density of the cured foam is 2.0 lbs./ft^3 and the temperature of the cavity reaches 70°C.

Calculating Stack Emissions:

Estimating emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined if the following information is known:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the "tack free" or "string" time during the curing process.

The enclosed process losses can be estimated from the following expression:

$$\mathbf{L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * M_w * K_{mdi}}$$

Where:

L_{fd}	=	the emissions from the enclosed process in lb/year.
V_{air}	=	the annual volume of displaced air in ft^3/year.
T_{proc}	=	the process temperature in °K. This is the maximum temperature of MDI "tack free" time.
VP_{mdi}	=	the vapor pressure of MDI in mm Hg. at process temperature
M_w	=	250.26 (this is the molecular weight of MDI).
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0^oC and 1-atmosphere.

Step I: Calculate the Annual Volume of Displaced Air (V_{air})

V_{air}	=	Annual material usage (M_a) / Foam Density (F_d)
V_{air}	=	(1,500,000 lbs./year) / 2.0 lbs/ft^3
$\mathbf{V_{air}}$	**=**	**750,000 ft^3/year**

Step II: Determine Process Temperature in ^oK

^oK	=	(^oC =+273.15)
^oK	=	(70 + 273.15)

^{o}K = 343.15

Step III: <u>Determine Vapor Pressure of MDI @ 343.15 ^{o}K</u>

MDI Vapor Pressure Chart (Vp_{mdi}) is 1.34 x 10^{-3} mm Hg

Step IV: <u>Determine Adjustment Factor</u> (K_{mdi})

A 50/50 mixture of MDI/PMDI from the Adjustment Factor Chart Table II K_{mdi} is 0.61.

Therefore:

L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * M_w * K_{mdi}

L_{fd} = (750,000 ft^3/year)(1/359)(273.15/343.15)(1.34x10^{-3}mmHg/760mmHg) (250.26)(0.61)

L_{fd} = 0.455 lb/year

6.0 Belt & Tire Cord Manufactures:

A MDI/PMDI mixture is used in belt manufacturing as a hardener. In the manufacture of belts, part of the process is to run synthetic cords through a vat solution containing a MDI/PMDI and toluene mixture and then passed it through an oven to activate the bonding process between the synthetic cord and isocyanate and dry the cord coating. The off-gases from the oven are passed through an incinerator or combustion device for destruction. Depending upon the process, the synthetic cord then goes through a number of various mixture dips and oven treatments. Once the cords have been treated, they are wound on spools for use in the belt building process.

The typical process consists of synthetic cords (60 - 100strands) averaging between 1/16 inch to ¼ inch) are passed through a vat solution containing a 15% solution of MDI/PMDI and toluene. The cords then pass through an oven that is heated to 250-280 ^{o}F. The length of the oven is 30 feet in length. While the cords are being processed in the oven, the MDI/PMDI impregnates the cords and reactively bonds with the cord fibers. The excess solution of toluene and MDI/PMDI is evaporated off. The off gas of the oven is passed through a combustion device to destroy excess solvent and MDI/PMDI mixture or vented to the atmosphere. The cords pass through another vat solution containing a hardener and toluene. The cords then passed through another oven at 450-480 ^{o}F. The off gas from the oven is used a make up air for the first oven with the excess air being diverted through a combustion device. Once the cords have been treated and cooled, they are wound on spools for use in the belt building process. The cords are processed at a rate of 175 ft./hr. and can go through a number of dipping solutions. The process runs for 24 hours a day 5 days a week.

The estimated MDI emissions can be calculated by taking the actual operating conditions for the application into consideration.

The controlling parameters that influence the emission rate are the temperature, flow rate and concentration of the exit gas stream. The worst-case scenario is that the exit gas stream is be saturated with all the MDI that is available. Actual operating conditions showed that the exit temperature of the stack was 250 °F and 8500 cfm and the cords were fed at a rate of 175 ft./hr. The length of the oven is 30 ft.. The amount of MDI/PMDI in the feed is 15% with the actual concentration of MDI in the MDI/PMDI feedstock being 50%. The MDI emissions can be calculated using the following formula:

L = $(V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * C_f * R_{MDI}$

Where:

L	=	the emissions in lb/hr.
V_{air}	=	the exhaust airflow rate in ft^3/min.
T_{sp}	=	the exhaust temperature in °K.
C_{mdi}	=	the MDI concentration, in ppmv, in the exhaust air.
M_W	=	the molecular weight of MDI (250.26).
K_{MDI}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
C_f	=	per cent MDI/PMDI in solution
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
C_{mdi}	=	$(VP_{MDI}/760) \times 10^6$
VP_{MDI}	=	MDI vapor pressure at exhaust temperature.
R_{MDI}	=	Unreacted fraction of MDI

Where:

R_{MDI} = $e^{(-k * t_R)}$

Where:

R_{MDI}	=	the unreacted fraction of MDI
k	=	the first order reaction rate constant in min^{-1}
t_R	=	the reaction time in minutes.

Therefore:

L	=	the emissions in lb/hr.
V_{air}	=	8500 ft^3/min.
T_{sp}	=	250 °F = 394.3 °K
M_W	=	250.26
K_{MDI}	=	0.69
C_f	=	15%
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
VP_{MDI}	=	0.08788 mm.
C_{mdi}	=	$(0.08788/760) \times 10^6 = 115.6$ ppmv
R_{MDI}	=	$e^{(-k * t_R)}$
k	=	the first order reaction rate constant in min^{-1}
t_R	=	the reaction time in minutes. (Total residence time in oven)
t_R	=	(30 ft x 2)/175 ft/hr = 0.34 hr = 21 mim.[5]
R_{MDI}	=	0.001 (assuming complete reaction is 99.9%)

5 The cord passes through 30 feet of oven at a temperature of 280 ºF and then another 30 feet where the cords are cooled before going through a second vat solution. Though the reaction is complete after 30 feet, a worst-case scenario is to assume completion is done after the cord exits the oven.

Solving for k :

$k = 0.329 \text{ min}^{-1}$

If we substitute the k constant in the equation we will find the free amount of MDI at the midpoint of the reaction is 0.0316 or that the reaction is 96.84% complete.

Substituting the values into the equation the emissions per hour are:

$$L = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * C_f * R_{MDI}$$

$$L = (8500/359)*(273.15/394.3)* (60)* (115.6/1000000)*(250.26)*(0.69)*(0.15)*(0.0316)$$

$L = 0.093$ Lbs./hr

This represents the maximum emission rate at steady state conditions prior to the exhaust stream being treated. The entire concentration profile of the free MDI can be calculated and plotted assuming a first order reaction mechanism. Plotting the un-reacted profile and taking the area under the curve we find that the effective unreacted fraction is 0.146 or 85.4% completion. Therefore,

L	=	the emissions in lb/hr.
V_{air}	=	8500 ft^3/min.
T_{sp}	=	250 °F = 394.3 °K
M_W	=	250.26
K_{MDI}	=	0.69
C_f	=	15%
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
VP_{MDI}	=	0.08788 mm.
C_{mdi}	**=**	**(0.08788/760) x 10^6 = 115.6 ppmv**
R_{MDI}	=	e^(-k * t_R)
k	=	the first order reaction rate constant in min^{-1}
t_R	=	the reaction in minutes. (Total resonance time in oven)

t_R = (30 ft x 2)/175 ft/hr = 0.34 hr = 21 mim.[4]

$R_{MDI} = 0.146$

Substituting the values into the equation the emissions per hour are:

$$L = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * C_f * R_{MDI}$$

$$L = (8500/359)*(273.15/394.3)* (60)* (115.6/1000000)*(250.26)*(0.69)*(0.15)*(0.146)$$

$L = 0.426$ Lbs./hr (before control)

$L = 0.426$ lbs/hr x 24 hrs/day x 5 days/wk x 52 wks/yr.

$L = 2658$ lbs/yr. Before control and reaction completion of 84.4%

The value above represents the emission rate before control. The standard control method in the Belt & Tire Cord Industry is incineration. If we assume a worst case scenario of only 85% control efficiency, the emission rate after control will be:

L	=	0.426 Lbs./hr x 0.15 = 0.064 lbs./hr.)
L_y	=	0.064 lbs./yr x 24 hr/day x 5 days/yr. X 52 weeks/yr.
L_y	=	399 lbs./yr. (This assumes no excess of MDI in Solution)

If we assume that the MDI present in the vat solution does not react with the cord fibers the maximum emission rate can be calculated with the formula:

L = $(V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * C_f * R_{MDI}$

Where:

L	=	the emissions in lb/hr.
V_{air}	=	the exhaust airflow rate in ft^3/min.
T_{sp}	=	the exhaust temperature in °K.
C_{mdi}	=	the MDI concentration, in ppmv, in the exhaust air.
M_W	=	the molecular weight of MDI (250.26).
K_{MDI}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
C_f	=	per cent MDI/PMDI in solution
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
C_{mdi}	=	$(VP_{MDI}/760) \times 10^6$
VP_{MDI}	=	MDI vapor pressure at exhaust temperature.
R_{MDI}	=	Unreacted fraction of MDI

Therefore:

L	=	the emissions in lb/hr.
V_{air}	=	8500 ft^3/min.
T_{sp}	=	250 °F = 394.2 °K
M_W	=	250.26
K_{MDI}	=	.69
C_f	=	15%
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
VP_{MDI}	=	0.08788 mm.
C_{mdi}	=	$(0.08788/760) \times 10^6 = 115.6$ ppmv
R_{MDI}	=	1.0
L	=	$(V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * C_f$
L	=	(8500/359)*(273.15/394.2)*(115.6/1000000)*(250.26)*(.69)*(.15)*(60)*(1)
L	**=**	**2.94 Lbs./hr (Worst case: No reaction/No control)**

If the amount of excess of MDI present in the vat solution is known then this can be factored into the equation. However, based upon the above set of conditions the maximum emission rate can not exceed 2.94 lbs/hr or 25,754 lbs/year based upon 8760 hrs/yr.

7.0 Boardstock (Open Process)

Releases of MDI will be calculated for a laminate boardstock manufacturing facility that uses 1,300,000 pounds of MDI-based component of a rigid foam system each year. MDI/PMDI component is shipped to the facility in tank trucks and is transferred to a 5,000-gallon (rail car-larger producers) indoor storage tank that is temperature controlled. The MDI component product is transferred to 2,000 lb. capacity "day tanks" which are stored inside the producing facility. Both the storage tanks and day tanks are kept at a constant temperature of 77°F (25°C). The contents of the "day tanks" are pumped through a metered foam machine and then delivered, mixed with the polyol, additives, blowing agent and other ingredients of the rigid foam system, and applied to the bottom facer of the moving laminate conveyor line. The laminate conveyor passes through a heated oven where the temperature is kept at a constant temperature of 180 °F. The "tack-time" is 5 seconds. Assume that the hot air in the oven passes over the laminate surface once at a rate of 5 meters /sec. The facility produces laminate boardstock that is on average 2 in. thick by 4 ft. wide at the rate of 10 linear feet per minute. The operation takes place in an area that measures 150 ft. long x 25 ft. wide x 20 high (100,000 $ft.^3$). The air concentration in the workplace shows 0.001 ppm MDI. The building under goes 5 air changes per hour, and production operates 16 hours per day 250 days a year.

Calculating Stack Emissions:

Estimating emissions from open processes such as boardstock production, it is assumed that MDI will migrate from all exposed surfaces. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the "tack-free" time and the exposed surface area.

The calculation methodology involves four steps:

1. Determine partial pressure of MDI at "tack-free" time.
2. Determine exposed area.
3. Determine evaporation rate.
4. Apply adjustment factor.

The evaporation rate (in gr/day) is determined from the following expression:

$$\mathbf{W = 25.4 * VP_{mdi} * (M_w / T_{proc}) * (u)^{0.78} * S_A * t_{TF} * K_{mdi}}$$

Where:

W = the evaporation losses from the open process in gr/day.

VP_{mdi} = the vapor pressure of MDI in atm. at process temperature.

T_{proc} = the process temperature in °K. This is the maximum temperature of the MDI "tack free" time.

M_w = 250.26 (this is the molecular weight of MDI).

U = the airflow speed in m/sec. This is the airflow in the vicinity of the process.

S_A = the exposed surface area in M^2. (This is the exposed surface area per day. For boardstock production, the surface area can be determined from the dimensions of the board.

t_{TF} = the "tack-free" time in seconds. The default value is 5 sec.

K_{mdi} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Step I: Determine Total Exposed Area

The total exposed surface area (S_A) will be the total exposed surface area of foam that is generated each day, including the area of foam that is exposed when the foam is cut at the end of the conveyor line. The foam is substantially cured when it is cut into slabs at the end of the conveyor line. However, the cut end surface areas are included as a conservative measure to account for any small amount of unreacted MDI that may be trapped in the nearly cured foam cells and released when the foam is cut. The laminate conveyor passes through a heated oven where the temperature is kept at a constant temperature of 180 °F. The "tack-time" is 5 seconds. Assume that the hot air in the oven passes over the laminate surface once at a rate of 5 meters /sec. The facility produces laminate boardstock that is on average 2 in. thick by 4 ft. wide at the rate of 10 linear feet per minute.

Total length of foam (ft) produce/day =(Production time)(Rate)
Length of foam (ft./day) = (16 hours/day) (60 min./hour)(10 ft foam/Min.)
Length of foam (ft/day) = 9,600.

Surface Area = top surface + side surface + cut-end surface
Top surface = 9,600 ft length x 4 ft width
Top Surface = 38,400 ft^2
Side surface = 2 x 9,600 ft. x (2 inch/12 in)/ft
Side surface = 3,200 ft^2

Cut-end surface = 2(4-ft by 2-inch surfaces)are produced for each 8-ft board that is manufactured and cut
Cut-end surface = 2 x [4 ft x (2 in width/12 in/ft)](9,600 ft/8 ft)
Cut-end surface = 1,600 ft^2

Therefore, surface area is equal to:

Surface area (A) = 38,400 ft^2 + 3,200 ft^2 + 1,600 ft^2

Surface area (A) =43,200 ft^2 x $M^3/10.76\ ft^2$ = 4,013 M^2

Step II: Determine Vapor Pressure in Atmospheres @ T_{pros}

VP_{mdi} = the vapor pressure of MDI in atm. at process temperature.
VP_{mdi} = 4.361 x 10^{-3} mm/760mm
VP_{mdi} = 5.74 x 10^{-6} atm.

Step III: Determine the Process Temperature in ^oK

T_{proc} = (^oC + 273.15)
T_{proc} = 355.4 °K

Step IV: Determine Adjustment Factor K_{mdi}

From Adjustment Factor Chart K_{mdi} is 0.62 @ 356 °K

Therefore:

$$\mathbf{W = 25.4 * VP_{mdi} * (M_w / T_{proc}) * (u)^{0.78} * S_A * t_{TF} * K_{mdi}}$$

$$W = (25.4)\ (5.74 \times 10^{-6}\ \text{atm.})\ (250.26/355.4\ ^\circ\text{K})\ (5\text{m/sec})^{0.78}\ (4013\text{M}^2)(5\ \text{sec})\ (0.62)$$

W = 4.5 grms./day x 1 lb/454 grms. X 250 days/year

W = 2.3 lbs/year

8.0 Boats

Releases of MDI/PMDI will be calculated for a boat assembly that injects, through a static mixing nozzle, a mixture of resin, PMDI, MDI, and blowing agent into the space between the inner and outer hulls by way of a hull-stiffening form. This produces rigid urethane foam that provides buoyancy and insulation for the craft. The foam mixture is supplied to the boat manufactures via 2500-pound totes and these totes are stored in-doors where the temperature remains constant. The foam mixture is injected at a "tack free" or "string" time temperature of 160^{o}F (70^{o}C). There are 18 different boat models manufactured ranging from 12-16ft. runabouts to 100-150ft. yachts. The majority of boat manufactures produce boats ranging from 25-30 ft. in length and anywhere from 25-30 boats per day. The typical production is a boat 25ft in length, 27 boats per day operating 24 hours a day, 250 days a year. The foam is 2 inches thick, has an average density of 1.8 lbs./cu.ft., and the surface area of the hull is 350 ft.^{2}. Fresh air is pulled across the work area and exhausted through hull-stiffening stack. The operation is performed in an area that is 100ft. by 100 ft. by 40 ft. and has a MDI concentration of 0.001 PPM. Calculate the stack emissions.

Calculating Stack Emissions

Estimating the emissions from closed processes, when the volume of the mold is known or can be determined by calculating the total volume of air displaced from the operations at the temperature of the process. A reasonable worst-case estimate of emissions can be made based on the volume, number of pieces produced per year and the maximum temperature.

The enclosed process losses can be estimated from the following expression:

$$\mathbf{L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}}$$

Where:

L_c	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft^3/year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0^{o}C and 1-atmosphere.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

V_{air} = (Area/piece)(No. Pieces/year)(Thickness)

V_{air} = (350 ft^2)(27 pieces/day)(250 days/yr.)(2/12)ft

V_{air} = 3.94 x 10^5 ft^3/yr.

Step II: Calculate Maximum Process Temperature in ^oK

The maximum temperature is the oven temperature of 70 ^oC or;

T_{proc} = (273.15 + 70^oC)^oK

T_{proc} = 343.15 ^oK

Step III: Determine Vapor Pressure of MDI @ 341.15 ^oK (VP_{MDI})

The vapor pressure @ 343.15 ^oK is 1.340 x 10^{-3}mm

Step IV: Determine Adjustment factor (K_{MDI})

Adjustment factor @ 343.15^oK and 50% MDI is 0.61

Therefore:

L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}

L_C = (3.94 x 10^{+5} ft^3/yr.)(1/359)(273.15^oK /343.15^oK)(1.340 x 10^{-3}mm/760) (250.26)(0.61)

L_c = 0.2375 lbs. / year.

9.0 Carpet & Rug Underlay

The Carpet and Rug Industry incorporates isocyanate into the production process to enhance the quality and performance of the final product. The isocyanate feed, consisting of methylenebis (phenyl Isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI), is reacted with a blend of polyol and inorganic filler. This formulation is continuously applied to the carpet substrate on a moving conveyer belt. Upon curing, the polyurethane that is formed imparts elasticity, strength, and resistance to the carpet.

There are two basic process configurations for coating carpets with polyurethane formulations. The flow-on method is generally used to apply laminate adhesives or cushion formulations to carpet floor coverings and reactively binding yarn and fabric. The process consists of pre-mixing a polyol and inorganic filler and delivering it as a liquid stream to a mixing and frothing device where it is combined with MDI/PMDI. The formed polyurethane is distributed across the width of the backside of the textile fabric by a traversing positioning device. A reservoir of the mixture is maintained in contact with the backside of the fabric and a “doctoring” blade scrapes onto the fabric the desired amount of the polymerizing mixture. The “doctoring” blade also gauges and controls the gap of the desired thickness of the laminating layer. Once applied, the carpet is then passed through a heated oven for curing, cooled and collected on take-up rolls for storage.

The second method takes the pre-mixed polyol/filler and mixes it with MDI in a specially designed low-pressure mixing head. A reservoir of the mixture is maintained on the belt and the newly formed polyurethane is spread

across the width of a Teflon impregnated conveyor belt with the use of a traversing positioning device. The carpet is then continuously laid onto the polymerizing mixture and conveyed over heated platens where the carpet is heated until the polymerization is complete. The carpet is the cooled and collected on take-up rolls for further processing.

Process Description

A two-component system is used to produce a carpet backing which is applied to a substrate surface. Part A, representing 84% of the total formulation, is a mixture of polyol and inorganic filler. Part B, representing 16% of the total formulation, is a 50% MDI/PMDI isocyanate mixture. The mixture is continuously applied on a conveyor belt having a width of 8 feet and moving at a speed of 30 ft/minute. The application rate of the formulation is 2 lb/yd^2. The carpet production rate is 345,600 ft^2/day corresponding to a consumption rate of 76,800 lb/day of total formulation (12,288 lb/day of MDI/PMDI). The process temperature is 200 ^{o}F and the air gap above the conveyor belt is 6 inches. An air blower with a capacity of 20,000 ft^3/min (measured at 59 ^{o}F) discharges air at a temperature of 130 ^{o}F. The unit operates 6000 hours/year (250 days/year). Estimate the annual emissions of MDI using the proposed methods.

The methodology developed assumes that the application of the MDI formulation occurs on a conveyor belt that is essentially enclosed. An air blower maintains a slight negative pressure in the conveyor belt area by continuously exhausting air from the process area through a stack. The MDI emissions can be estimated by considering the air exhaust rate, the temperature of the exit gas, the reaction rate between the isocyanate and polyol resin, and the "effective" MDI concentration in the gas stream. A block diagram of the carpet coating operation is shown in figure III-1. As a worst-case scenario, it can be assumed that the air leaving the application area will be in thermodynamic equilibrium with the MDI present on the carpet. **This approach can be applied irrespective of how the polyurethane is applied to the carpet substrate.**

The emissions from carpet coating operation can be estimated from the following expression:

$$L_{cc} = (V_{air}/359)\ (60)\ (ppmv/1000000)\ (M_W)\ (K_{MDI})\ (C_{iso}/100)\ (t_{cc})\ (R_{MDI}) \quad (1)$$

Where:

L_{cc} = the emissions in lb/year for carpet coating operations.

V_{air} = the exhaust airflow rate in ft^3/min (at 32 ^{o}F = 0^{o}C).

ppmv = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure.

T_{st} = the temperature of the air leaving the stack in °K.

M_W = the molecular weight of MDI (250.26).

K_{MDI} = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of K_{MDI} is 1.00 for pure MDI.

C_{iso} = the % of isocyanate feedstock in the total formulation.

R_{MDI} = the unreacted fraction of MDI on the conveyor belt relative to the MDI initially present in the formulation. This value reflects the unreacted fraction of MDI present at the midpoint of the application process and is based upon a first-order reaction.

t_{cc} = the total time of operation in hours/year.

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0^{o}C and 1-atmosphere.

60 = time, minutes/hour.

A first order reaction can be expressed by the following reaction:

$$R_{mdi} = e^{-(k)\ (tR)} \quad (2)$$

Where:

R_{MDI} = the unreacted fraction of MDI
k = the first order reaction rate constant in min^{-1}
t_R = the reaction time in minutes

Solution:

V_{air} = 20,000 ft^3/min (at 59 ^oF) = 18,956 ft^3/min (at 32 ^oF)
T_{st} = 130 ^oF = 93.33 ^oC = 327.6 ^oK
VP_{mdi} = 2.879 x 10^{-4} mm Hg
ppmv = 2.879 x 10^{-4}/760 = 0.3788 ppmv
MW = 250.26
% MDI = 50
K_{mdi} = 0.59[6]
C_{iso} = 16 %
t_{cc} = 6000 hour/year

To determine the value of R_{mdi} the expression for the first-order reaction is used:

$R_{mdi} = e^{-(k)(tR)}$ (2)

Where:

R_{mdi} = the unreacted fraction of MDI
k = the first order reaction rate constant in min^{-1}
t_R = the reaction time in minutes

For a conversion of 99.9 %, R_{mdi} = 0.001 and t_R = 4.0 min

Substituting the appropriate values into Equation 2:

$0.001 = e^{-(k)(4.0)}$ $k = 1.727\ min^{-1}$

For t_R = 2.0 min $R_{mdi} = e^{-(1.727)(2.0)} = 0.031$

This value means that after 2 minutes (half the reaction time) about 97 % of the "free" MDI has polymerized and no longer contributes to the MDI emission

R_{mdi} = 0.03 (this value represents a typical unreacted fraction of MDI at the midpoint of the application process).

Substituting the appropriate values into Equation 1:

L_{cc} = (18,956 ft^3/min/359ft^3/lb-mole) (60min/hr) (0.3788ppmv/1000000) (250.26 lbs/lb-mole) (0.59) (16 parts MDI/100parts mixture) (0.03) (6000hrs. /yr.) (0.59)

L_{cc} = **4.73 lb/yr**

The annual consumption of MDI/PMDI = (12,288lbs./day) (250 days/yr.)

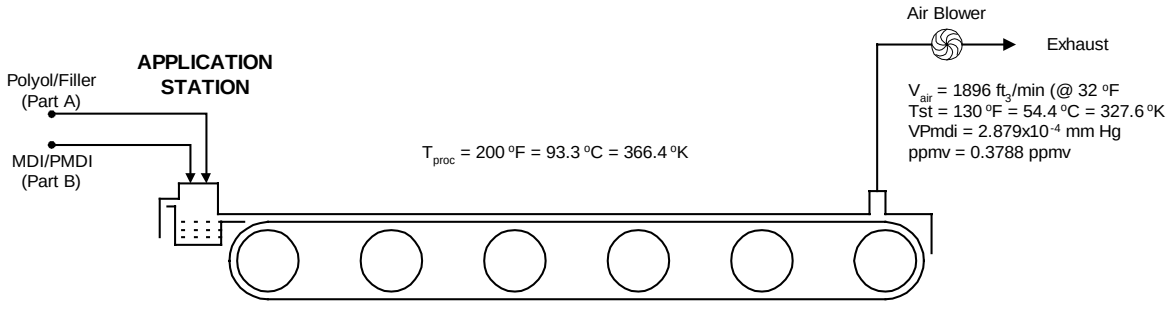
= **3,072,000 lb/yr isocyanate feedstock**

6 Values obtain from Appendix B Table II MDI/PMDI Adjustment Factor Chart.

Emission factor = MDI Emitted / lbs. MDI Processed

= 4.73/ 3,072,000

Emission factor = **1.54×10^{-6} lb MDI emission/lb isocyanate**



% MDI in isocyanate = 50 %
K_{mdi} = 0.59
C_{iso} = 16 %
t_{cc} = 6000 hr/yr = 250 days/yr
R_{mdi} = 0.03

Belt width = 8 ft
Belt speed = 30 ft/min
Air gap above belt = 6 inches
Application rate of formulation = 2 lb/yd^2
Formulation consumption = 76,800 lb/day
MDI/PMDI consumption = 12,288 lb/day
MDI/PMDI consumption = 3,072,000 lb/yr

FIGURE III-1
CARPET COATING OPERATION
BLOCK FLOW DIAGRAM

Alliance for the Polyurethane Industries

10.0. Doors

Methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol blend to provide insulation inside a doorframe. There are two approaches used in industry. One application will inject the two-component system through a spray nozzle inside the doorframe after the door has been assembled and allows the polyurethane to expand filling the closed cavity. The second application is to inject the two component system into the door cavity after the inner backing has been installed, place the outer backing on the frame, allowing the polyurethane to expand to the contour of the door framing while being pass through a oven. Once polyurethane has cured the door assembly is finished. In both cases the application is a closed cavity system.

Process Description

An assembly line produces a standard door at a rate of 340 doors per hour. The size of the door is 7 feet high 36 inches wide and two inches thick. Each door is injected with 5.4 lbs. of a 1/1 resin to Diisocyanate blend. The temperature of the mixture is 80^{o}F.

Calculating Stack Emissions

To estimate the emissions from closed processes, when the volume of the mold is known or can be determined, is calculated by determining the total volume of air displaced from the operations at the temperature of the process. A reasonable worst-case estimate of emissions can be made based on the volume, number of pieces produced per year and the maximum temperature.

The enclosed process losses can be estimated from the following expression:

$$\mathbf{L_C = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_W * K_{MDI}}$$

Where:

L_C = emissions lb./year.

V_{air} = annual volume of displaced air in ft^3/year.

T_{proc} = process temperature in °K. (maximum temperature of the MDI).

VP_{MDI} = vapor pressure of MDI in mm Hg at process temperature.

M_W = 250.26 (this is the molecular weight of MDI).

K_{MDI} = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0^{o}C and 1-atmosphere.

Step I: <u>Calculate Annual Volume of Displaced Air (V_{air})</u>

V_{air} = (Area/piece)(No. Pieces/year)(Thickness)

V_{air} = (21 ft^2)(340 pieces/hr.)(24 hr./day)(365 days/yr.)(2/12)ft

$\mathbf{V_{air} = 1.04\ 10^{+7} ft^3/yr.}$

Step II: <u>Calculate Maximum Process Temperature in ^{o}K</u>

The maximum temperature is the oven temperature of 80^{o}F or;

T_{proc} = 299.8^{o}K

Step III: Determine Vapor Pressure of MDI @ 299.8^{o}K (VP_{MDI})

The vapor pressure @ 299.8 ^{o}K is 1.23 x 10 $^{-5}$mm

Step IV: Determine Adjustment factor (K_{MDI})

Adjustment factor @ 299.8 ^{o}K and 25% MDI is 0.34

Therefore:

$$L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

$$L_C = (1.04 \times 10^{+7}\ ft^3/yr.)(1/359)(273.15^{o}K / 299.8^{o}K)(1.23 \times 10^{-5}mm/760)(250.26)(0.34)$$

L_c = .0365 lbs. / year.

11.0 Filling/Blending

A company fills a blend consisting of 40% MDI/PMDI and 60% dioctylphthalate into half-gallon containers. The operation fills 5,000 containers a day. The facility operates 250 days/year. The material is mixed in a reactor-blend tank at 70 ^{o}F and packaged at a temperature of 70 ^{o}F. The percent MDI in the feedstock is 50%. Calculate annual emissions.

Calculating Stack Emissions

Estimating emissions from a mixing/blending operation will correspond to the total volume of air displaced from the containers at the filling temperature. The reasonable worst-case scenario will be to assume that the volume of air displaced from the container is saturated with MDI/PMDI. Loses will be experienced when the reactor or blend tank is filled with the MDI/PMDI mixture and when the reactor/blend tank is emptied into containers. Loses will be based upon the volume of MDI/PMDI charged to the reactor/blend tank and the volume of containers filled with the blend.

The filling losses can be estimated from the following equation:

$$L_{fll} = V_{air} * (1 / 359) * (273.15 / T_{fill}) * (VP_{MDI} / 760) * M_w * K_{MDI} * C_{blnd}$$

Where:

L_{fll} = the emissions from the filling operation in lbs/year

V_{air} = the annual volume of displaced air in ft^3/year

T_{fill} = the temperature the material is charged or filled at in ^{o}K

VP_{MDI} = the vapor pressure of MDI in mm Hg at the charging/filling temperature.

M_w = the molecular weight of MDI (250.26)

K_{MDI} = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and/or blend and at the blending/filling temperature.

C_{blnd} = the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then C_{blnd} is 1.

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0^oC and 1-atmosphere.

To calculate the total emission we must determine what emission are contributed to the charging/filling of the reactor/blend tank and the emissions contributed from the discharge from the reactor/blend tank into the containers.

Step I: <u>Determine Volume Displaced by MDI/PMDI During Charging/Filling of Reactor/Blend Tank</u>

Assumption made is that the MDI/PMDI mixture is charged first and that the vapor space remains concentrated with MDI/PMDI during the charging of the dioctylphthalate (therefore presenting worst case scenario). The total volume of air displaced will be equal to the volume of containers filled.

Therefore:

V_{Tair} = (Number containers/year) * (Volume of container)
= (5,000 containers/day x 250 days/year) * (1/2 gallon)
= (625,000 gallons/year)/(7.48 gallons/ft^3)
V_{Tair} = 83,556 ft^3

Total Volume of air displaced by MDI/PMDI is 40 % of total volume:

V_{air} = V_{Tair} x %MDI/PMDI
V_{air} = (83,556 ft^3) (0.40)

V_{air} = 33,422 ft^3

Step II: <u>Determine Vapor Pressure at Charging/Blending Temperature</u> <u>*VP*$_{MDI}$</u>

***VP* @ 70 ^oF is 6.09 x 10^{-6} mm Hg**

Step III: <u>Determine Charging/Filling Temperature (T_{fill}) in ^oK</u>

T_{fill} is equal to 294.2 ^oK

Step IV: **<u>Determine Adjustment Factor K_{MDI}</u>**

The adjustment factor of 50% MDI/PMDI @ 294.2 ^oK is 0.54.

Step V: **<u>Determine C_{blnd}.</u>**

C_{blnd}. is equal to I.0.

Therefore:

$$\mathbf{L_{fll} = V_{air} * (1 / 359) * (273.15 / T_{fill}) * (VP_{MDI} / 760) * M_w * K_{MDI} * C_{blnd}}$$

L_{fll} = (83556 ft3) (1/359) (273.15/294.2) (6.09 x 10^{-6} mm Hg/760) (250.26) (0.54) (1)

$$\mathbf{L_{fll} = 2.379 \times 10^{-4} \text{ lbs/year}}$$

Part II: Determine Losses from the Filling of Containers

The losses from the filling of the containers can be found from the following equation:

$$\mathbf{L_{fll} = V_{air} * (1 / 359) * (273.15 / T_{fill}) * (VP_{MDI} / 760) * M_w * K_{MDI} * C_{blnd}}$$

Where:

L_{fll} = the emissions from the filling operation in lbs/year
V_{air} = the annual volume of displaced air in ft^3/year
T_{fill} = the temperature the material is charged or filled at in ^oK
VP_{MDI} = the vapor pressure of MDI in mm Hg at the charging/filling temperature.
M_w = the molecular weight of MDI (250.26)
K_{MDI} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and/or blend and at the blending/filling temperature.
C_{blnd} = the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then C_{blnd} is 1.

Step I: Determine Volume Displaced by the Filling of Containers

The total volume of air displaced will be equal to the volume of containers filled.

Therefore:

V_{Tair} = (Number containers/year) * (Volume of container)
= (5,000 containers/day x 250 days/year) * (1/2 gallon)
= (625,000 gallons/year)/(7.48 gallons/ft^3)
$\mathbf{V_{Tair}}$ = **83,556 ft^3**

Step II: Determine Vapor Pressure at Charging/Blending Temperature VP_{MDI}

***VP* @ 70 ^{o}F is 6.09 x 10^{-6} mm Hg**

Step III: Determine Charging/Filling Temperature (T_{fill}) in ^oK

T_{fill} is equal to 294.2 ^oK

Step IV: **Determine Adjustment Factor K_{MDI}**

The adjustment factor of 50% MDI/PMDI @ 294.2 ^{o}K is 0.54.

Step V: **Determine C_{blnd}.**

C_{blnd}. is equal to 0.40

Therefore:

L_{fll} = V_{air} * (1 / 359) * (273.15 / T_{fill}) * (VP_{MDI} / 760) * M_w * K_{MDI} * C_{blnd}

L_{fll} = (83,556 ft^3) (1/359) (273.15/294.2) (6.09 x 10^{-6} mm Hg/760) (250.26) (0.54) (.40)

L_{fll} = 9.51 x 10^{-5} lbs/year

Therefore total annual lost is equal to losses from charging/filling of the reactor/blend tank and the annual losses from filling the containers.

L_{fll} = $L_{f\ charging}$ + $L_{f\ filling}$

L_{fll} = (2.379 x 10^{-4} lbs/year) + (9.51 x 10^{-5} lbs/year)

L_{fll} = 3.33 10^{-4} lbs/year

12.0 Foundry & Casters

Stack emissions from the process used by foundries & Casters can be estimated using (1) material balance or (2) engineering calculations.

Material Balance

TERMS:

% Reacted means:

The amount of this chemical that reacts during the curing process and no longer exists as this chemical after curing.

% Evaporated means:

The amount of this chemical that evaporates (becomes airborne) during the mold/core-making process.

% Remaining in Mold/Core Means:

The amount of this chemical that, even after curing/reacting, still remains in its original form in the finished product.

ASSUMPTIONS :

A phenolic urethane coldbox binder is used to make cores. This binder consists of two components; Part I and Part II. During the course of a year you have used 400,000 pounds of Part I and 325,000pounds of

Part II. The two-component system is injected into the mold at ambient temperature (20 °C) and the exhaust temperatures of the hot ore pour and shakedown systems are 110 °C and 22 °C respectfully. The exhaust blowers are rated at 20,000 cfm and 50,000 cfm respectfully. The reaction goes to 99.99% completion. The Material Safety Data Sheets (MSDS) shows the each component consists of the following:
Part I consists of :

Phenol (6%),
Naphthalene (1.98%),
Formaldehyde (0.3%),
Biphenyl (0.08%)
Trimethylbenzene (2.08%),
Xylene (0.44%),
Cumene (0.16%)

Part II consists of:

MDI (39.95%)
Naphthalene (4.06%)
Xylene (0.2%)
Biphenyl (0.08%).

Since the percentages of Xylene, Cumene and Biphenyl in Part I and the percentages of Xylene and Biphenyl in Part II are below the SARA de minimis level (1% for non-carcinogens and 0.1% for carcinogens) no inventory or further calculations for these chemicals from this binder are necessary.

Step I: Calculate Inventory:

The amount of chemical in binder will equal the percentage amount times the amount of binder used.

Part I Chemicals:

Chemical	%	Lbs. Used	Lbs. Chemical
Phenol	6	400,000	24,000
Trimethylbenzene	2.08	400,000	8,320
Naphthalene	1.98	400,000	7,920
Formaldehyde	0.3	400,000	1,200

Part II Chemicals:

Chemical	%	Lbs. Used	Lbs. Chemical
MDI	39.95	325,000	29,838
Naphthalene	4.06	325,000	13,195

Step II: Determine Amount Reacted, Evaporated, Encapsulated in Core

Coldbox Process:

Part I Chemicals:

Chemical	% Reacted	% Evaporated	% Remaining
Phenol	90	0	10
Naphthalene	0	50	50

Part II

MDI	99.99	0	0.01
Naphthalene	0	50	50

Step III: Calculate amounts of chemical Reacted, Evaporated, and Remained in the Core

This is done by multiplying the pounds of the chemical by the percentage. Therefore:

Chemical	Reacted	Evaporated	Remaining
Phenol	21,600	0	2,400
MDI	129,825	0	13
Naphthalene	0	10,558	10,588

The amount of MDI lost due to emissions is 13 lbs.

Note: Most foundries vent the cold boxes to an acid scrubber. The unreacted MDI that can be lost due to core production would be hydrolyzed in the scrubber solution. The amount of MDI encapsulated in the core could only be lost during core and mold shakeout and amount of material that is vaporized would depend upon the shakeout temperature.

Engineering Calculations

Core Box Step:

During this step the MDI formulation is injected into the mold at ambient temperature. The losses will correspond to the total volume of air displaced from the molds at the filling temperature. A reasonable worst-case estimate of filling losses can be made based on the total volume of MDI formulation consumed, the composition of the MDI formulation and the injection temperature.

The core box losses can be estimated from the following expression: [font change]

$$L_{cb} = V_{air} * (1 / 359) * (273.15 / T_{cb}) * (VP_{mdi} / 760) * MW * K_{mdi} * C_{iso}/100$$

Where:

L_{cb} = the emissions from the core box step in lb/year.

V_{air} = the annual volume of displaced air in ft^3/year (at the filling temperature).

T_{cb} = he filling temperature in °K.

VP_{mdi} = the vapor pressure of MDI in mm Hg. at the filling temperature..

MW = the molecular weight of MDI (250.26).

K_{mdi} = an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature..

C_{iso} = the % of isocyanate feedstock in the total formulation. If only MDI/PMDI material is

filled then C_{iso} = 100%.

Therefore:

L_{cb} = V_{air} * (1 / 359) * (273.15 / T_{cb}) * (VP_{mdi} / 760) * MW * K_{mdi} * C_{iso}/100

V_{air} = 400,000 lbs Part 1 + 325,000 lbs Part 2= 725,000 lbs x 1 gal/10 lbs x 1 $ft.^3$/7.45 gal.

V_{air} = 9692 ft^3/yr.

T_{cb} = the filling temperature in °K = 20 °C + 273.15 °K = 293.15 °K

VP_{mdi} = the vapor pressure of MDI in mm Hg @20 °C = 5.28 x 10^{-6} mm Hg.

MW = the molecular weight of MDI (250.26).

K_{mdi} = an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature. 100 pure MDI is used in the feedstock K =1.0

C_{iso} = the % of isocyanate in the total formulation. 325,000 lbs x 39% / 725,000lbs

C_{iso} = 0.04

L_{cb} = (9692 ft3/yr.)*(1/359)*(273.15/293.15)*(5.28 x10^{-6}/760)*(250.26)*(1)*(.04)

L_{cb} = 1.80 x 10^{-6} lbs./yr.

Mold Pour and Shakeout Step

During the ore pour and shakeout step, exhaust air blowers are used to maintain a slight negative pressure in the process area by continuously sucking air and exhausting it to the atmosphere through a series of exhaust stacks. Residual MDI is thus removed from the mold and the sand. For this situation the MDI emissions can be estimated by considering the air exhaust rate, the temperature of the exit gas, the residual free MDI in the mold, and the "effective" MDI concentration in the gas stream. As a worst-case scenario, it can be assumed that the air leaving the process area will be in thermodynamic equilibrium with the free MDI remaining in the mold.

The losses from the mold pour and shakeout step can be estimated from the following expression:

L_{so} = (V_{air}/359) * (60) * (ppmv/1000000) * (MW) * (K_{mdi}) * (C_{iso}/100) * (t_{so}) * (F_{mdi})

Where:

L_{so} = the emissions in lb/year from the shakeout and mold pour step.

V_{air} = the exhaust airflow rate in ft^3/min (at stack temperature).

ppmv = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure.

MW = the molecular weight of MDI (250.26).

K_{mdi} = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of K_{mdi} is 1.00 for pure MDI.

C_{iso} = the % of isocyanate feedstock in the total formulation.

F_{mdi} = the fraction of free MDI remaining in the mold. The free MDI is assumed to be 0.01 (1% of the initial MDI remains unreacted during this step).

T_{so}	=	the total time of operation in hours/year.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
60	=	time, minutes/hour.

Mold Pour:

L_{mp}	=	the emissions in lb/year from the mold pour step.
V_{air}	=	the exhaust airflow rate in ft^3/min (at stack temperature).
ppmv	=	the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure.
MW	=	the molecular weight of MDI (250.26).
K_{mdi}	=	adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of K_{mdi} is 1.00 for pure MDI.
C_{iso}	=	the % of isocyanate feedstock in the total formulation.
F_{mdi}	=	the fraction of free MDI remaining in the mold. The free MDI is assumed to be 0.01 (1% of the initial MDI remains unreacted during this step).
T_{so}	=	the total time of operation in hours/year.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
60	=	time, minutes/hour.

Where:

V_{air}	=	20,000 cfm*(273.15°K /383.15 °K) = 14,258 acfm
ppmv	=	(0.03898/760)*(1,000,000) = 51.3 ppmv
MW	=	250.26
K_{mdi}	=	1.0
C_{iso}	=	(29,838lbs MDI/725,000 lbs Total feed) = .04
F_{mdi}	=	0.0001
T_{so}	=	8760 hours/year.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
60	=	time, minutes/hour.

Therefore:

L_{mp} = (14,258 acfm)*(60min/hr)*(51.3ppmv/1000000)*(250.26)*(0.04)*(1.0)* (8760)* (0.0001)

L_{mp} = 1.07 lbs/year

Using the same approach for the shakeout Step, the estimated emissions are:

L_{so}	=	the emissions in lb/year from the shakeout and mold pour step.
V_{air}	=	the exhaust airflow rate in ft^3/min (at stack temperature).
ppmv	=	the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure.
MW	=	the molecular weight of MDI (250.26).

K_{mdi}	=	adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of K_{mdi} is 1.00 for pure MDI.
C_{iso}	=	the % of isocyanate feedstock in the total formulation.
F_{mdi}	=	the fraction of free MDI remaining in the mold. The free MDI is assumed to be 0.01 (1% of the initial MDI remains unreacted during this step).
T_{so}	=	the total time of operation in hours/year.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
60	=	time, minutes/hour.

Where:

V_{air}	=	50,000 cfm*(273.15°K /295.15 °K) = 46,273 acfm
ppmv	=	(0.00000682/760)*(1,000,000) = 0.0090 ppmv
MW	=	250.26
K_{mdi}	=	1.0
C_{iso}	=	(29,838lbs MDI/725,000 lbs Total feed) = .04
F_{mdi}	=	0.0001
T_{so}	=	8760 hours/year.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
60	=	time, minutes/hour.

Therefore:

L_{so} = (46,273 acfm)*(60 min/hr)*(0.009ppmv/1000000)*(250.26)*(0.04)*(1.0)*(8760)*(0.0001)

L_{so} = 6.12 x 10^{-4} lbs/year

Total Emissions = **L_{cb} + L_{mp} + L_{so}**

Total Emissions = 1.80 x 10^{-6} lbs./yr. + 1.07 lbs/year + 6.12 x 10^{-4} lbs/year

Total Emissions = 1.07 lbs./year

13.0 Laminator (Cavity)

Methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol blend in the manufacture of laminator boardstock. A two component system, using a polyol blend (Component A) is mixed with a MDI/PMDI mixture (Component B) through a special designed nozzle is dispersed onto laminator backing, enclosed between an upper and lower plate, and passed through an oven for curing. This produces rigid foam sheeting that is cut to desired length and width.

Process Description:

A two component system, (Component A: Polyol mixture; Component B: MDI/PMDI mixture), is dispersed onto

a laminator boardstock backing, forming a polyurethane, at a rate of 52 lbs./min.. This is passed through an oven at an average temperature of 123^{o}F. The line runs at a rate of 16 Ft^{2}/piece with an average board thickness of 1.60 inches and produces 24 pieces/min.. The temperature of the ISO is 93^{o}F containing a 1/1 ratio of MDI to PMDI**.**

The emissions from open processes can be estimated, when the volume of the mold is known or can be determined, by calculating the total volume of air displaced from the operations at the temperature of the process. A reasonable worst-case estimate of emissions can be made based on the volume, number of pieces produced per year and the maximum temperature.

The enclosed process losses can be estimated from the following expression:

$$\mathbf{L_C = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_W * K_{MDI}}$$

Where:

L_C	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft^{3}/year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_W	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	**=**	the molar volume of an ideal gas in ft^{3}/lb-mole @ 0°C and 1-atmosphere.

Step I: <u>Calculate Annual Volume of Displaced Air (V_{air})</u>

Blend Consumed = (52 lbs/min) (60 min/hr) (24 hr/day) (365 days/year)

= 27,331,200 lbs/year

V_{air} = (Area/piece)(No. Pieces/year)(Thickness)

V_{air} = (16 ft^{2})(24 pieces/min)(60 min/hr)(24 hr./day)(365 days/yr.)(1.6/12)

$\mathbf{V_{air} = 2.68 \times 10^{+7}\ ft^3/yr.}$

Step II: <u>Calculate Maximum Process Temperature in ^{o}K</u>

The maximum temperature is the oven temperature of 123^{o}F or;

$\mathbf{T_{proc} = 323.7^{o}K}$

Step III<u>: Determine vapor Pressure of MDI @ 323.7 ^{o}K (VP_{MDI})</u>

The vapor pressure @ 323.7^{o}K is 1.92 x 10^{-4}mm

Step IV<u>: Determine Adjustment factor (K_{MDI})</u>

Adjustment factor @ 323.7 ^{o}K and 25% MDI is 0.38

Therefore:

L_C = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}

L_C = (2.68 x 10^{+7} ft^3/yr.)(1/359)(273.15^{o}K /323.7^{o}K)(1.92 x 10^{-4}mm/760)(250.26)(0.38)

L_C = 1.534 lbs. / year.

14.0 Mobile Homes/Motor Homes

Releases of MDI/PMDI will be calculated for a mobile home assembly facility that produces mobile homes that are insulated with MDI-based rigid foam. The facility uses a total of 2,000,000 pounds of MDI/PMDI feedstock that comprise rigid foam "system." The "system" includes an MDI/PMDI-containing component and a polyol/catalyst/blowing agent component. The MDI/PMDI component is purchased in bulk and stored indoors in a 6,000-gallon tank at 25^{o}C. MDI is transferred to 550-lb. day tank as needed. The day tank is stored indoors. The MDI is pumped directly from the day tanks to the foam mixer head. It may be difficult to estimate the cavity size of each mobile home that is filled with rigid foam insulation. MDI releases can instead be estimated from the target foam density for the insulation and the total quantity of foam feedstock that are used in the year.

Calculating Stack Emissions

To estimate the emissions from closed processes, when the volume of the mold is known or can be determined, is calculated by determining the total volume of air displaced from the operations at the temperature of the process. A reasonable worst-case estimate of emissions can be made based on the volume of Polyol and MDI/PMDI used per year at the maximum temperature.
The enclosed process losses can be estimated from the following expression:

L_C = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}

Where:

L_C	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft^3/year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

Step I: <u>Calculate Annual Volume of Displaced Air (V_{air})</u>

V_{air} = (4,000,000 lbs./year)/(10 lbs./gal.) (1 gal/7.48 ft^3)

V_{air} = 53,469 ft^3

Step II: <u>Calculate Maximum Process Temperature in ^{o}K</u>

The maximum temperature is the oven temperature of 77 ^{o}F or;

$$\mathbf{T_{proc} = 298.2\ ^{o}K}$$

Step III: <u>Determine vapor Pressure of MDI @ 299.8 ^{o}K (VP_{MDI})</u>

The vapor pressure @ 298.2^{o}K is 1.00 x 10^{-5}mm

Step IV: <u>Determine Adjustment factor (K_{MDI})</u>

Adjustment factor @ 298.2 ^{o}K and 25% MDI is 0.33

Therefore:

$$\mathbf{L_C = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}}$$

$$L_C = (5.35 \times 10^4\ ft^3/yr.)(1/359)(273.15^{o}K /298.2^{o}K)(1.00 \times 10^{-5}mm/760)(250.26)(0.33)$$

$$\mathbf{L_C = 1.51 \times 10^{-4}\ lbs./\ year.}$$

15.0 Packaging

Methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol blend in the packaging of equipment, appliances, machine parts etc. to protect them from getting damaged. The system consist of two parts: Part A being polyol and Part B diisocyanate mixture. The two parts are mixed in a customized system that mixes within the dispenser head and material dispersed into a container or cavity containing the equipment, appliance, machine parts etc. The container is then placed on a conveyor and transported to the warehouse for storage.

A facility uses 10 million pounds of Polyol/MDI/PMDI blend for the packaging of machine parts to ship to Europe. The MDI/PMDI is stored in a 10,000-gallon storage tank and maintained at 25 ^{o}C. The Polyol/MDI/PMDI blend in injected into the containers inside an assembly room (50 ft. wide x 50 ft. long x 15 ft. high) that is vented through the roof. Since the container size varies, the targeted density of the foam is 1.5 lbs./ ft^3. Determine the stack emissions.

To estimate emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the "tack free" or "string" time during the curing process

The enclosed process losses can be estimated from the following expression:

$$L_{pk} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_{pk} = emissions lb./year.

V_{air} = annual volume of displaced air in ft^3/year.

T_{proc} = process temperature in °K. (maximum temperature of the MDI).

VP_{MDI} = vapor pressure of MDI in mm Hg. at process temperature.

M_w = 250.26 (this is the molecular weight of MDI).

K_{MDI} = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

Step I: Calculate Annual Volume of Displaced Air (V_{air})

V_{air} = (Amount of material processed/year)/Foam Density

V_{air} = $(10.0 \times 10^{+6}$ lbs./year)/(1.5 lbs./ft^3

V_{air} = $6.6 \times 10^{+6}$ ft^3/yr.

Step II: Calculate Process Temperature in ^oK

The process temperature is of 25 ^oC or;

T_{proc} = 298.15^oK

Step III: Determine Vapor Pressure of MDI @ 298.15 ^oK (VP_{MDI})

The vapor pressure @ 298.15 ^oK is 1.072×10^{-5}mm

Step IV: Determine Adjustment factor (K_{MDI})

To determine adjustment factor (K_{MDI}) , the percent of MDI in the blend must be determined. The ratio of Polyol to MDI/PMDI is 1/1. Therefore, the percentage of MDI/PMDI is:

%MDI/PMDI = (1/(1+1) * 100
%MDI/PMDI = 50 %

The percent MDI in the MDI/PMDI mixture is 52%. Therefore the percent MDI in the blend is equal to

%MDI = (51.8) * (50.0)
%MDI = 25.0

Adjustment factor @ 298.7 ^oK and 25.0% MDI is 0.33

Therefore:

L_{pk} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}

L_{pk} = $(6.6 \times 10^{+6}$ ft^3/yr.)(1/359)(273.15^oK /298.15^oK)$(1.072 \times 10^{-5}$mm/760)(250.26)(0.33)

L_{pk} = 0.0188 lbs. / year.

16.0 Rebond

Methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate are used in a binder mixture that enables fabric and sponge-like material to bond into one solid flexible mass. This material can be cut to form carpet backing and underlay.

Process Description

A binder mixture containing polyol/MDI is added to a closed reactor system already charged with fluff (cut foam). Live steam is injected into the mixture at 60 psig for a period of 2.5 minutes. Steam is being exhausted from bottom and top of reactor through blower system. Binder mixture contains 40% MDI. Reactor produces a log that is 5' diameter and 10' high. System averages 10 logs per hour using 60 pounds of binder per log.

Calculating Stack Emissions

This is a unique process that combines the two-component system of Polyol and MDI and uses steam to produce the polyurethane foam. The amount of MDI lost can be calculated using the enclosed cavity equations.

The total amount of emissions emitted will correspond to the total volume of air displaced at the temperature of the process. A reasonable worst-case estimate of emissions can be made based upon the volume of the mold cavity, the number of pieces produced per year, and the maximum process temperature.

The enclosed process losses can be estimated from the following expression:

$$\mathbf{L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}}$$

Where:

L_c	=	emissions from the enclosed process in lb./year.
V_{air}	=	the annual volume of displaced air in ft^3/year.
T_{proc}	=	the temperature material is dispensed at in °K.
VP_{MDI}	=	the vapor pressure of MDI in mm Hg. at dispensed temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

Step I: <u>Calculate Annual Volume of Displaced Air (V_{air})</u>

V_{air}	=	Annual Consumption x Density
V_{air}	=	1,344,000 lbs/year / 10 lbs/gal/7.48 gal/ft^3
$\mathbf{V_{air}}$	=	$\mathbf{1.783 \times 10^4\ ft^3/year}$

Step II: <u>Calculate Maximum Process Temperature in ^oK</u>

The maximum temperature is the oven temperature will be the temperature of 60 psig steam. The temperature of 60 psig (75psi) is 425.9^{o}K. Therefore:

T_{proc} = **425.9 ^{o}K**

Step III: <u>Determine vapor Pressure of MDI @ 425.9^{o}K (VP_{MDI})</u>

The vapor pressure @ 425.9^{o}K is 7.034 x 10 $^{-1}$mm

Step IV: <u>Determine Adjustment factor (K_{MDI})</u>

Adjustment factor @ 425.9 ^{o}K and 40% MDI is 0.57

Therefore:

L_C = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI}/ 760) * M_w * K_{MDI}

L_C = (1.783^{+4}ft^3/yr) (1/359) (273.15/425.9)^{o}K) (7.034 x 10 $^{-1}$mm/760 mm)(254.38) (0.57)

L_C = **4.27 lbs. per year**

Note: This presents worst-case scenario because it does not assume that the steam hydrolyzes any of the MDI/PMDI.

17.0 Spandex

One of the unique ways polyol and diisocyanate are used is in the manufacture of spandex. Polyol and a mixture of MDI/PMDI are reacted with amines to form a segmented polyurethane. Using a special technique a final product is obtained from a "dry-spinning" operation. To control emissions a scrubber system is installed to control emissions of silicon oils, various pre-polymers and other VOC's.

Process Description

A reactor system is charged with dimethylacetamide (DMAC), amines, methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture, and silicon oils. Reactor is heated to 150 ^{o}F and a blended polyol is added over a period of two hours. The reaction forms a segmented polyurethane which, through a "dry-spinning" process, producers a spandex material. The reactor is equipped with a water scrubber to remove VOC's including any unreacted MDI/PMDI. The scrubber has an exhaust blower and operates at a temperature between 20 – 40 ^{o}C. The blower operates at 8000 scfm. MDI is charged in 2% excess (total charge of MDI per batch is 600 lbs.). Two batches are run at the same time. Plant operates 24 hours a day 365 days a year. The facility process 5.7 million pounds of MDI.

Calculating Stack Emissions

The stack emissions are based upon the excess amount of MDI charged per batch and the efficiency of the scrubber. Most water scrubbers are 99 % efficient in hydrolyzing MDI. We will assume that the unreacted MDI will hydrolyze except 1%. The remaining unreacted MDI will volatilize according to the scrubber temperature.

The amount of MDI emitted to the atmosphere from the scrubber can be determined from the following equation:

L_S = V_{air} * (1/359) * (273.15/T_S) * (VP_{MDI}/760) * M_w

Where:

V_{air} = the annual volume of displaced air through the scrubber in ft^3/year
T_S = the maximum scrubber temperature
VP_{MDI} = the vapor pressure of MDI at maximum scrubber operating temperature ^oK
M_W = the molecular weight of MDI (250.26)
359 = **the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.**

Step I: <u>Calculate the Annual Displacement of Air by the Scrubber (V_{air})</u>

Blower operates at 8000 cfm. Total air displaced per year is equal to the following:

V_{air} = **(**8000 ft^3/min) (60 min/hr) (8760 hr/year)
V_{air} = 4.20 x 10^{+9} ft^3/year

Step II: <u>Determine Maximum Scrubber Temperature in ^oK (T_S)</u>

^oK = (^oC + 273.15)
^oK = (40 + 273.15)
^oK = 313.15

Step III: <u>Determine the Vapor Pressure of MDI @ 313.15 ^oK from Chart</u>

The vapor pressure of MDI @ 313.15 is 8.76 x 10^{-4} mm

Step IV: <u>Determine the partial pressure of MDI in air as it leaves the Scrubber</u>

Conservatively we can assume that the mole fraction of MDI leaving the scrubber is 0.001.

Partial pressure of MDI is equal to 8.76 x 10^{-4} mm x 0.001 or 8.76 x 10^{-7} mm

Therefore:

$L_S = V_{air} * (1/359) * (273.15/T_S) * (VP_{MDI}/760) * M_W$

L_S = (4.20 x 10^{+9} ft^3/year) (1/359) (273.15/313.15) (8.76 x 10^{-7} mm/760) (250.26)

L_S = 2.59 lbs/year

18.0 Spray Foam

Methylene*bis* (phenyl isocyanate) (MDI) and polymeric diphenylmethane diisocyanate (PMDI) mixture is used in conjunction with a polyol blend to provide insulation inside motor home roof caps. This mixture is injected into the cavity walls to form the insulation barrier between the inner and outer wall. Part A being polyol and Part B diisocyanate mixture. The two parts are mixing in a customized system that mixes within the dispenser head and material dispersed into a cavity or back of roof frame.

Process Description

A two component system, (Component A: Polyol mixture; Component B: MDI/PMDI mixture), is dispersed into the motor home roof cap forming a polyurethane foam insulation at a rate of 42 lbs./hr. The temperature of the ISO is 78 ^{o}F containing a 1/1 ratio of Polyol to MDI/PMDI. The targeted foam density is 2.0 lbs./ft^3.

Calculating Stack Emissions

To estimate emissions from open processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the "tack free" or "string" time during the curing process.

The enclosed process losses can be estimated from the following expression:

$$\mathbf{L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}}$$

Where:

L_{fd}	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft^3/year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	**=**	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

Step I: <u>Calculate Annual Volume of Displaced Air (V_{air})</u>

V_{air}	=	(Amount of material processed/year)/Foam Density
V_{air}	=	(42 lbs./hr)(8760 hr./year)(1/2.0 lbs./ft^3
V_{air}	=	1.84 x 10^{+5} ft^3/yr.

Step II: <u>Calculate Process Temperature in ^{o}K</u>

The process temperature is 78^{o}F or;

T_{proc} = 298.7^{o}K

Step III: Determine Vapor Pressure of MDI @ 298.7 ^{o}K (VP_{MDI})

The vapor pressure @ 298.7^{o}K is 1.071 x 10^{-5}mm

Step IV: Determine Adjustment factor (K_{MDI})

A Blend of 50/50 of MDI/PMDI at a ratio of 1/1 of Polyol to MDI/PMDI yields a composition of 25% MDI. Therefore,

Adjustment factor @ 298.7 ^{o}K and 25% MDI is 0.33

Therefore:

L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_W * K_{MDI}

L_{fd} = (1.81 x 10^{+5} ft^3/yr.)(1/359)(273.15^{o}K /298.7^{o}K)(1.071 x 10^{-5}mm/760)(250.26)(0.33)

L_{fd} = 5.454 x 10^{-4} lbs. / year.

19.0 Spray Booth

A spray coating operation, carried out in the Specialty Products Section, spray coats automotive parts in a spray booth. The exhaust temperature is 90 ^{o}F and the blower air exhaust rate is 10,000 cfm. The percentage of MDI in the spray mix is 33%. The total annual spray time was 1000 hours.

The exhaust airflow rate and the temperature at which the spray coating is carried out will govern the emissions associated with a spray booth operation. If the concentration of the exit gas is not known , the worst-case scenario is to assume that the air is saturated with MDI/PMDI at the exit temperature.

The emissions from spray coating operations can be estimated from the following expression:

$$L_{sp} = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * t_{sp}$$

Where:

L_{sp}	=	the emissions in lb/year for spray coating operations.
V_{air}	=	the exhaust airflow rate in ft3/min.
T_{sp}	=	the spray temperature in °K.
C_{mdi}	=	the MDI concentration, in ppmv, in the exhaust air.
M_W	=	the molecular weight of MDI (250.26).
K_{MDI}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
t_{sp}	=	is the total time in hours/year that spray coating is occurring.
359	**=**	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

C_{mdi} = $(VP_{MDI}/760) \times 10^{6}$

VP_{MDI} = MDI vapor pressure at exhaust temperature.

Therefore:

L_{sp}	=	emissions in lb/year.
V_{air}	=	10,000 ft^3/min.
T_{sp}	=	305.4 °K.
C_{mdi}	=	0.0319 ppmv
M_W	=	250.26.
K_{MDI}	=	0.41
t_{sp}	=	1000 hours/year that spray coating is occurring.

Substituting the values into the equation:

L_{sp} = 4.94 lbs./year

20.0 Oriented Strand Board (OSB) Manufactures:

Methylene*bis* (phenyl isocyanate) (MDI) is used as a binder in the production of particleboard. The process consists of four steps:

Step I: Wood chips, straw, wheat, hays, or other grains are grounded up and conveyed into moisturizing chamber. Water is either added or removed to produce moisture content of 10-13%.

Step II: The mixture of woodchips and water is transferred into second chamber where MDI is added at a weight equivalent to 3.0 -3.9 %. Chamber is a closed system with no vent..

Step III: The combination of wood, water and MDI is mixed and then spread over a "cold plate" frame that forms a 8-inch matting. The “cold plate” moves along a conveyor system where between 5-6 frames are loaded onto a press where a hydraulic system compresses the mixture to a desired thickness between 1/4" to 5/8", while heating the "cold plate" to a temperature of 175 -180 ^{o}C. During this step the MDI reacts with the water to form a polyurethane bond with the fiber. The press is open and the trapped carbon dioxide is released. The press is equipped with a blower system that vents to the roof. The temperature of the exit gases range between 90-140 ^{o}F.

Step IV: The formed boards are removed from the press, checked for quality, trimmed to 4'x8' sheets, and stacked for shipping.

The controlling parameters that influence the emission rate are the temperature, flow rate and concentration of the exit gas stream. The worst-case scenario is that the exit gas stream is saturated with MDI. Actual operating conditions showed that the exit temperature of the stack was 140 °F and 8400 cfm. The amount of MDI/PMDI in the feed is 10% with the actual concentration of MDI 50%. The facility operates 24/7.

The estimated MDI emission can be calculated using the following formula:

$L = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * C_f$

Where:

L	=	the emissions in lb/hr.
V_{air}	=	the exhaust airflow rate in ft^3/min.
T_{sp}	=	the exhaust temperature in °K.
C_{mdi}	=	the MDI concentration, in ppmv, in the exhaust air.
M_W	=	the molecular weight of MDI (250.26).
K_{MDI}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
C_f	=	per cent MDI/PMDI in solution
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
C_{mdi}	=	$(VP_{MDI}/760) \times 10^6$
VP_{MDI}	=	MDI vapor pressure at exhaust temperature.

Therefore:

L	=	the emissions in lb/hr.
V_{air}	=	8400 ft^3/min.
T_{sp}	=	140 °F = 333.2 °K
M_W	=	250.26
K_{MDI}	=	.60
C_f	=	3.9%
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
VP_{MDI}	=	0.00005071 mm.
C_{mdi}	=	$(0.00005071/760) \times 10^6 = 0.6672$ ppmv
L	=	$(V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * C_f$
L	=	(8400/359)*(273.15/333.2)*(.6672/1000000)*(250.26)*(.60)*(.039)*(60)
L	=	.0045 Lbs./hr
L	=	.0045 Lbs./hr x 8760 hrs/yr
L	**=**	**40 lbs/yr.**

21.0 Water Heaters

A water heater assembly facility that produces water heaters insulated with MDI-based rigid foam uses a total of 6,000,000 pounds of feedstocks that comprise a rigid foam "system." The "system" includes an MDI/PMDI-containing component and a polyol/catalyst/blowing agent component. The MDI/PMDI component is purchased in bulk and stored indoors in a 60,000-gallon tank. The tanks are filled 65 times each year. The temperature of the MDI storage tank does not exceed 25^{o}C and only drops 20^{o} on an average a day. MDI is transferred to 400 lb. day tank as needed. The day tanks are stored indoors and temperature is maintained at 25^{o}C. The MDI is pumped directly from the day tanks to the foam mixer head. The density of the foam is 1.9 lbs/ft^{3}. It may be difficult to estimate the cavity size of each water heater that is filled with rigid foam insulation. MDI releases can instead be estimated from the target foam density for the water heater insulation and the total quantity of foam feedstocks that are used in the year.

Calculating Stack Emissions

To estimate emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year can be determined from the following:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the "tack free" or "string" time during the curing process.

The enclosed process losses can be estimated from the following expression:

$$\mathbf{L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}}$$

Where:

L_{fd}	=	emissions lb./year.
V_{air}	=	annual volume of displaced air in ft^{3}/year.
T_{proc}	=	process temperature in °K. (maximum temperature of the MDI).
VP_{MDI}	=	vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	=	the molar volume of an ideal gas in ft^{3}/lb-mole @ 0°C and 1-atmosphere.

Step I: <u>Calculate Annual Volume of Displaced Air (V_{air})</u>

V_{air} = (Amount of Material Processed/year)/Foam Density

V_{air} = (6.0 x 10^{+6} lbs./year)/(1.9 lbs./ft^{3}

$\mathbf{V_{air}}$ = **3.2 x 10^{+6} ft^{3}/yr.**

Step II: <u>Calculate Process Temperature in ^{0}K</u>

The process temperature is of 78 ^{o}F or;

T_{proc} = 298.7 ^{o}K

Step III: Determine vapor Pressure of MDI @ 298.7 ^{o}K (VP_{MDI})

The vapor pressure @ 298.7 ^{o}K is 1.072 x 10 $^{-5}$mm

Step IV: Determine Adjustment factor (K_{MDI})

To determine adjustment factor (K_{MDI}) , the percent of MDI in the blend must be determined. The ratio of Polyol to MDI/PMDI is 1/1. Therefore, the percentage of MDI/PMDI is:

%MDI/PMDI = (1/(1+1) * 100
%MDI/PMDI = 50 %

The percent MDI in the MDI/PMDI mixture is 52%. Therefore the percent MDI in the blend is equal to

%MDI = (51.8) * (50.0)
%MDI = 25.0

Adjustment factor @ 298.7 ^{o}K and 25.0% MDI is 0.33

Therefore:

L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_{w} * K_{MDI}

L_{fd} = (3.16 x 10^{+6} ft^3/yr.)(1/359)(273.15^{o}K /298.7^{o}K)(1.072 x 10^{-5}mm/760) (250.26) (0.33)

L_{fd} = 0.00953 lbs. / year.

Overall Facility Example

The basic formulas presented in the preceding pages, can be used to estimate the amount of air emissions from a facility that handles an MDI and /or MDI/PMDI mixture. Typically the total air emissions will be the sum of the amounts emitted from the following:

- Storage and Day Tanks (working and breathing losses)
- Fugitive Emissions (non-point sources) Measured
- Fugitive Emissions(non-point Source) Equipment Leaks
- Stack Emissions from Enclosed Processes
- Stack Emissions from Open Processes
- Stack Emissions from Continuous Processes
- Stack Emissions from Saturated Air Stream

Although the above list represents the predominant sources of air emissions from most facilities, each facility and process is unique. One needs to consider whether there are other potential emission sources (both fugitive and point source emissions).

The example presented below utilizes the techniques described in the above-mentioned categories. In each case the worst-case scenario is used for illustration.

Example:

J & J Foam Products, Inc. operates a facility that processes 10 MMlb/yr of MDI/PMDI. Shipments are received by rail car and are off-loaded into a 40,000-gallon storage tank. Operations include:

1. Re-packaging of material from storage into 55-gallon drums,
2. Manufacture of automotive sun visors,
3. Manufacture of seat cushions,
4. Spray coating of bumpers and fenders, and
5. Manufacturing of laminated boardstock used in the construction industry.

Fugitive emissions from the process area include measured air exhaust concentration and from equipment leaks located outside.

The facility had two spills during the year that resulted in a loss of 1000 gallons of material.

Process Details:

10 MM Lbs. of MDI/PMDI a year are received by rail car. The product is off-loaded into a 40,000-gallon storage tank located outdoors. Average annual air temperature is 68 ^{o}F with an average daily temperature range of 18 °F.

The total manufacturing area measures 200 ft. by 300 ft. by 30 ft. (1.8 million cu.ft.). The air exchange rate is 5 per hour. The operation manufactures 24 hours per day 365 days per year. The outside operation consists of a closed system that has 1000 connectors, 8 pumps, 25 light liquid valves, 4 agitators, and 4 safety relief valves. The annual average air temperature was reported to be 78 ^{o}F.

The facility makes sun visors for the automotive industry. The average size sun visor is 2 ft. long by 6 inches wide and 2 inches thick (0.17 cu.ft.). The company produces 1.5 million parts using a closed mold two-component system of MDI/PMDI and polyol resin (1:1 ratio). The process is carried out at a temperature of 85 ^{o}F.

2 MM lbs. of MDI/PMDI are used to produce seat cushions. The polyol and isocyanate are mixed through a special head at 85 °F at a ratio of 1:1. The foam density of the cushion is 2.0 lbs./cu.ft.

Laminated boardstock 8 feet long by 4 feet wide and 2 inches thick is produced at a rate of 17 ft/min. The temperature of the exit air is 85 ^{o}F. The wind velocity across the surface of the board was measured at 3 ft/sec. Tack time is one minute. The line operates 24 hours per day 7 days per week.

MDI/PMDI is repackaged at 75 ^{o}F into 55 gallon drums each one weighing 500 pounds net. Total pounds re-packaged 1 MM lbs.

Shipping cartons are assembled using an adhesive mixture containing 2% MDI. The adhesive is applied using a special roller applicator that covers 20,000 sq.ft./day. The plant operates 5 days/week (250 days/year). The material is applied at 275 ^{o}F and the exposed area is subject to an airflow velocity of 5 meters/second. Tack-time is 10 seconds.

A spray coating operation, carried out in the Specialty Products Section, spray coats automotive parts in a spray booth. The exhaust temperature is 90 ^{o}F and the blower air exhaust rate is 10,000 cfm. The percentage of MDI in the spray mix is 33%. The total annual spray time was 1000 hours.

During the course of the year the facility had a number of spills. Total amount of material spilled was 1000 gallons that resulted in exposed area 1000 sq.ft. for 20 hours. The evaporation temperature was 85 ^{o}F and the airflow velocity was 20 miles/hour. The percent of MDI in the material was 50.

Estimate the total emissions of MDI/PMDI.

To estimate the total emissions will require calculating the emission from the following:

1. Storage: Working and Breathing Loses
2. Fugitive: Measured and Equipment Leaks
3. Process: Closed Cavity, Foam Density, and Continuous
4. Filling/Blending Operation
5. Adhesives
6. Spray Coating
7. Spill

1. Storage: Working and Breathing Loses

Working losses occur when MDI/PMDI vapor that is present over the liquid in a storage tank is displaced from the tank by the addition of MDI/PMDI liquid during tank filling. Reasonable worst case estimate of working losses can be made based on the size and number of storage tanks, the average storage temperature, and the number of times each tank is filled in one year.

The working losses can be estimated from the following expression:

$$\mathbf{L_W = Q_W * (1 / 359) * (273.15 / T_{amb}) * (Vp_{amb} / 760) * M_W * K_{mdi}}$$

Where:

L_W	=	the working losses in lb/year.
Q_W	=	the annual throughput of MDI pumped to the tank in ft^3/year.
T_{amb}	=	the storage temperature in °K.

Vp_{amb}	=	the vapor pressure of MDI at the storage temperature in mm Hg
M_W	=	the molecular weight of MDI (250.26).
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the storage temperature.
359	**=**	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

Substituting the following values into the equation:

L_W	=	lbs./year
Q_W	=	1,000,000 gallons/yr. = 133,681 ft^3/year.
T_{amb}	=	68 ºF = 293.2 °K.
Vp_{amb}	=	5.2 x 10^{-6} mm Hg
M_W	=	250.26
K_{mdi}	=	0.54 @ 293. 2 °K, 50% MDI
L_W	**=**	**3.256 x 10^{-4} lb./yr.**

The breathing losses can be estimated from the following expression:

L_B	**=**	**$365 * M_{air} * (VP_{amb} / 760) * M_W * K_{mdi}$**
M_{air}	**=**	**$(V_V / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb})$**
V_V	**=**	**$V_T * (100\text{-}L_T)$**
K_E	**=**	**T_R / T_{amb}**

Where:

L_B	=	the breathing losses in lb/year.
M_{air}	=	the total air displaced per day in lb-mole/day.
VP_{amb}	=	the vapor pressure of MDI at the ambient temperature in mm Hg
M_w	=	the molecular weight of MDI (250.26).
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
V_V	=	the daily average vapor space of the storage tank in gallons
V_T	=	the capacity of the storage tank.
T_{amb}	=	the average ambient temperature in °K.
T_R	=	the average day-night temperature fluctuation in °K.
K_E	=	the vapor expansion factor due to day-night temperature fluctuation.

Substituting the following values into the equations:

L_B	=	breathing losses in lb/year.
VP_{amb}	=	5.2 x 10^{-6} mm Hg
M_W	=	250.26
K_{mdi}	=	0.54.
V_V	=	20,000 gallons

V_T = 40,000 gallons.
T_{amb} = 293.2 °K.
T_R = 10 °K.
K_E = 10 °K/293.2 °K = 0.0341.

V_v = V_T * (100-L_T) = 20,000 gallons
K_E = T_R / T_{amb} = 0.0341
M_{air} = (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb}) = 3.33×10^{-3} lb-mole/day
L_B = 365 * M_{air} * (VP_{amb} / 760) * M_w * K_{mdi}

L_B = 8.0×10^{-7} lb./yr.

Therefore;

LT = L_W + L_B

L_T = 3.256×10^{-4} lb./yr. + 8.0×10^{-7} lb./yr.

L_T = 3.26×10^{-4} lb./yr

2. Fugitive Emissions: Measured and Equipment Leaks

Fugitive emissions are air releases of volatile chemicals that typically occur due to leaks from fittings and seals in chemical process equipment, transfer operations or storage systems. Direct measurement or monitoring data can be used to estimate fugitive emissions. In the absence of direct measurement or monitoring data, industrial hygiene data on MDI concentrations in the workplace can be used to estimate MDI or MDI/PMDI fugitive emissions. This technique can only be used if the industrial hygiene data are representative of average concentrations throughout the year and throughout the building.

Measured Fugitive Emissions:

The fugitive emissions can be estimated from the following expression:

$$\mathbf{L_{fg} = C_{mdi} * (V_B / 359) * N_{year} * (273.15 / T_{amb}) * M_w * K_f}$$

Where:

L_{fg} = the fugitive emissions in lb/year.
C_{mdi} = the average MDI concentration, in ppmv, in the air within the building.
V_B = the volume of the workspace building in ft^3.
N_{year} = the number of air exchanges per year.
T_{amb} = the ambient temperature in °K.

M_w = the molecular weight of MDI (250.26).
K_f = an adjustment factor to the MDI concentration in the building air. API uses a value of 1.10
359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

Therefore:

C_{mdi} = 0.001ppm = 1.0×10^{-9}
V_B = 1,800,000 ft^3
N_{year} = 43,800 per year
T_{amb} = 298.2 °K.
M_w = 250.26.
K_f = 1.10

Therefore:

L_{fg} = $(1.0 \times 10^{-9}) * (1{,}800{,}000\ ft^3/359) * (43{,}800) * (273.15/298.2) * (250.26) * (1.1)$

L_{fg} = 56.33 lbs/year.

Fugitive Emissions: Equipment Leaks

In cases where monitoring data is not available, EPA has developed a method using emission factors based upon the type of fittings and number of fittings used in the process. The methodology used for MDI/PMDI is an adaptation of an EPA Correlation Method ("1995 Protocol for Equipment Leak Emission Estimate" - EPA-453/R-95-017). The method presented here uses the actual formulas recommended by the EPA except that saturated vapor concentrations are used instead of screening values. Since the vapor concentration of MDI cannot exceed the saturation vapor pressure at a given temperature, the predicted screening values are limiting and conservative values. The calculation methodology involves the following steps:

1. Determine the saturated concentration of MDI.
2. Calculate emission factor for each equipment type.
3. Determine emissions for each equipment type.
4. Determine total losses from equipment leaks.

The MDI emissions from equipment leaks using the Modified Correlation Approach can be determined using the following equations:

SV = $1{,}315.8 \times 10^{[(10.902 - 4634.09/(266.15 + t)]}$

Where:

SV = Screening Value in ppmv and
t = Temperature in ^oC.

The calculated Screening Value (SV) is then inserted into the Leak Rate/Screening Value Correlation Formula for the appropriate equipment type (found in Table V-6) and the leakage rate is determined.

Table V-6
Leak Rate/Screening Value Correlations

Equipment Type	Correlation Leak Rate (kg/hr) ($a*(SV)^b$)
Gas Valve	$1.87x10^{-06}$ x $(SV)^{0.873}$
Light Liquid Valve	$6.41x10^{-06}$ x $(SV)^{0.787}$
Light Liquid Pump [c]	$1.90x10^{-05}$ x $(SV)^{0.824}$
Connectors	$3.05x10^{-06}$ x $(SV)^{0.885}$

Table V-7
Equipment leak Emission Factors lbs/hr-component @ 78 ^oF

Equipment Type	Temp. ^oF	Vapor Pressure (mm Hg)	Screening Value (SV) (ppmv)	Equation Constant (a)	Equation Constant (b)	Emission Factor[1] (lb./hr)[3]
Gas Valves	**78**	$1.0720x10^{-04}$	$1.41x10^{-02}$	$1.87x10^{-06}$	**0.873**	$9.992x10^{-08}$
Light Liquid Valves	**78**	$1.0720x10^{-04}$	$1.41x10^{-02}$	$6.41x10^{-06}$	**0.797**	$4.941x10^{-07}$
Light Liquid Pumps	**78**	$1.0720x10^{-04}$	$1.41x10^{-02}$	$1.90x10^{-05}$	**0.824**	$1.251x10^{-06}$
Connectors	**78**	$1.0720x10^{-04}$	$1.41x10^{-02}$	$3.05x10^{-06}$	**0.885**	$1.548x10^{-07}$

Equipment Type	Service	Number Components	Adjustment Factor	Emissions (lbs/hr)	Emissions (lbs./year)
Valves	**Light Liquid**	25	0.55	$4.941x10^{-07}$	0.0593
Pumps	Light Liquid	16	0.55	$1.251x10^{-06}$	0.09608
Connectors	All	1000	0.55	$1.548x10^{-07}$	0.7433
				Total	**0.8987**

Total Fugitive emissions due to emissions from process area and outside:

$$L_{fg} = 56.33 \text{ lbs/year} + 0.8987 \text{ lbs./year} = 57.23 \text{ lbs./year}$$

3. Process: Closed Cavity

The manufacture of sun visors represents a closed system. Since the cavity size and the number of parts manufactured in a year are known, the emissions can be estimated using the following equation:

$$L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{MDI} / 760) * M_w * K_{MDI}$$

Where:

L_c = emissions lb./year.
V_{air} = annual volume of displaced air in ft^3/year.
T_{proc} = process temperature in °K. (maximum temperature of the MDI).
VP_{MDI} = vapor pressure of MDI in mm Hg. at process temperature.

M_w = 250.26 (this is the molecular weight of MDI).

K_{MDI} = adjustment factor.

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

V_{air} = V_{pc} x N_{pc}

V_{pc} = volume displace per piece

N_{pc} = number of pieces

Therefore:

V_{air} = annual volume of displaced air in ft^3/year.

T_{proc} = 302.6°K..

VP_{MDI} = 1.733×10^{-5} mm Hg. at process temperature.

M_w = 250.26 (this is the molecular weight of MDI).

K_{MDI} = 0.56

V_{air} = V_{pc} x N_{pc}

V_{pc} = 0.17 $ft.^3$

N_{pc} = 1,500,000 pieces

L_C = 2.031×10^{-3} lb./year

Process: Closed Foam Density

To estimate the emissions for the manufacture of seat cushions, the formula to estimate emissions for a closed system given the foam density is used. The equation is:

$$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * MW * K_{mdi}$$

Where

L_{fd} = the emissions from the enclosed process in lb/year.

V_{air} = the annual volume of displaced air in ft^3/year.

T_{proc} = the process temperature in °K. This is the maximum temperature of the MDI "tack free" time.

VP_{mdi} = the vapor pressure of MDI in mm Hg. at process temperature.

M_w = 250.26 (this is the molecular weight of MDI).

K_{mdi} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

359 = **the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.**

Therefore:

$$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * MW * K_{mdi}$$

Where

L_{fd}	=	lbs./year
V_{air}	=	4,000,000 lbs./ 2.0 lbs./ft^3 = 2,000,000 ft^3 /year.
T_{proc}	=	302.6°K.
VP_{mdi}	=	1.733 x 10^{-5} mm Hg.
M_w	=	250.26
K_{mdi}	=	0.34
L_{fd}	**=**	**9.759 x 10^{-3} lb./year**

Process: Open Process(continuous):

To estimate the emissions from the laminated boardstock process, the formula for the Open Process (continuous) can be used.

The calculation methodology involves four steps:

1.Determine partial pressure of MDI at "tack-free" time.
2. Determine exposed area.
3. Determine evaporation rate.
4. Apply adjustment factor.

The evaporation rate (in gr/day) is determined from the following expression:

$$W = 25.4 * VP_{mdi} * (M_w / T_{proc}) * (u)^{0.78} * SA * t_{TF} * K_{mdi}$$

Where

W	=	the evaporation losses from the open process in gr/day.
VP_{mdi}	=	the vapor pressure of MDI in atm. at process temperature.
T_{proc}	=	the process temperature in °K. This is the maximum temperature of the MDI "tack free" time.
M_w	=	250.26 (this is the molecular weight of MDI).
u	=	the airflow speed in m/sec. This is the airflow in the vicinity of the process.
SA	=	the total exposed surface area in M^2/day. This includes top and all sides.
t_{TF}	=	the "tack-free" time in seconds..
K_{mdi}	=	the adjustment factor.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Therefore:

VP_{mdi}	=	2.281 x 10^{-8} atm.
T_{proc}	=	302.6°K
M_w	=	250.26 (this is the molecular weight of MDI).
u	=	0.91m/sec.
SA	=	10,234 M^2.(This includes top and all sides).
t_{TF}	=	60 seconds..
K_{mdi}	=	0.56.

Substituting the values into the equation:

W = 0.152 grams/day
W = (0.152 grms./day)(365 days/year) (1 lb./454 grms.)
W = 0.125 lb./year

4. Calculating Emissions from Mixing/Blending/Filling Process

Estimating emissions from a filling operation will correspond to the total volume of air displaced from the containers at the filling temperature. The reasonable worst-case scenario will be to assume that the volume of air displaced from the container is saturated with MDI/PMDI.

The filling losses can be estimated from the following equation:

$$L_{fll} = V_{air} * (1 / 359) * (273.15 / T_{fill}) * (VP_{MDI} / 760) * M_w * K_{MDI} * C_{blnd}$$

Where:

L_{fll} = the emissions from the filling operation in lbs/year
V_{air} = the annual volume of displaced air in ft^3/year
T_{fill} = the temperature the material is charged or filled at in ^oK
VP_{MDI} = the vapor pressure of MDI in mm Hg at the charging/filling temperature.
M_w = the molecular weight of MDI (250.26)
K_{MDI} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and/or blend and at the blending/filling temperature.
C_{blnd} = the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then C_{blnd} is 1.
359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

Therefore:

L_{fll} = emissions lbs/year
V_{air} = 13,368 ft^3/year
T_{fill} = 297 ^oK
VP_{MDI} = 8.692 x 10 -6 mm Hg.
M_w = 254.38
K_{MDI} = 0.55
C_{blnd} = 1.0

Substituting the values into the equation, the estimated emissions from the filling operation is:

L_{fll} = 5.34 x 10 $^{-5}$ lb./year

5. Process; Adhesive

MDI will migrate from all exposed surfaces and all losses will be the result from evaporation. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the "tack-free" time and the exposed surface area.

The calculation methodology involves the following steps:

1. Determine partial pressure of MDI at "tack-free" temperature.
2. Determine the exposed area.
3. Determine evaporation rate.

The evaporation rate (in grams/day) is determined from the following expression:

$$\mathbf{W = 25.4 * VP_{MDI} * (M_W / T_{proc}) * (u)^{0.78} * S_A * t_{TF}}$$

Where:

W	=	the evaporation losses from the open process in gr./day.
VP_{MDI}	=	the vapor pressure of MDI in atmospheres @ process temperature.
T_{proc}	=	the process temperature in °K.
M_W	=	the molecular weight of MDI
u	=	the airflow speed in m/sec.
S_A	=	the exposed surface area in M^2.
t_{TF}	=	the "tack-free" time in seconds.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

Therefore:

W	=	losses in gr./day.
VP_{MDI}	=	4.155×10^{-5} atmospheres
T_{proc}	=	380.4 °K.
M_W	=	250.26
u	=	5 m/sec.
S_A	=	1858 m^2.
t_{TF}	=	5 seconds.

Substituting the values into the equation, the estimated emissions from applying the adhesive is:

W	=	22.7 grms./day
W	=	(22.7grms./day)(250days/year) (1 lb./454 grms.)
W	**=**	**12.5 lb./year**

6. Process: Spray Coating

The exhaust airflow rate and the temperature at which the spray coating is carried out will govern the emissions associated with a spray booth operation. If the concentration of the exit gas is not known , the worst-case scenario is to assume that the air is saturated with MDI/PMDI at the exit temperature.

The emissions from spray coating operations can be estimated from the following expression:

$$\mathbf{L_{sp} = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * t_{sp}}$$

Where:

L_{sp}	=	the emissions in lb/year for spray coating operations.
V_{air}	=	he exhaust airflow rate in ft3/min.
T_{sp}	=	the spray temperature in °K.
C_{mdi}	=	the MDI concentration, in ppmv, in the exhaust air.
M_W	=	the molecular weight of MDI (250.26).
K_{MDI}	=	an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
t_{sp}	=	the total time in hours/year that spray coating is occurring.
359	**=**	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
C_{mdi}	=	$(VP_{MDI}/760) \times 10^6$
VP_{MDI}	=	MDI vapor pressure at exhaust temperature.

Therefore:

L_{sp}	=	emissions in lb/year.
V_{air}	=	10,000 ft^3/min.
T_{sp}	=	305.4 °K.
C_{mdi}	=	0.0319 ppmv
M_W	=	250.26.
K_{MDI}	=	0.41
t_{sp}	=	1000 hours/year that spray coating is occurring.

Substituting the values into the equation:

$$\mathbf{L_{sp} = 4.94\ lbs./year}$$

7. Spills:

A liquid chemical accidentally spilled onto the ground may spread out over an area, vaporize and cause an air emission. Such accidental releases must be reported under section 313. Evaporative losses from spills (and other open processes) depend on a number of factors including:

1. The volatility of the material
2. The size of the spill
3. The temperature of the surrounding area
4. The wind speed
5. The time that the liquid from the spill is allowed to evaporate

A fairly simple model proposed by the EPA that accounts for all these factors is provided by the following equation:

$$\mathbf{Q_R = (0.284/82.05) * (u)^{0.78)} * A_{spill} * (VP_{MDI}/T_{spill}) * (M_W)^{2/3} * K_{mdi}}$$

Where:

Q_R	=	the evaporation rate in lb/min.
u	=	the airflow speed in m/sec. This is the airflow in the vicinity of the process.
A_{spill}	=	the area of the spilled material in ft^2
VP_{mdi}	=	the vapor pressure of MDI in mm Hg. at the spill temperature.
T_{spill}	=	the average evaporation temperature in °K.
M_W	=	the molecular weight of MDI (250.26).
Kmdi	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The spill losses can be determined by multiplying the evaporation rate (QR) in lb/min by the time the spill is on the ground and converting the calculated value to the desired units:

$$\mathbf{L_{spill} = Q_R * t_{spill} * (60)}$$

Where:

L_{spill}	=	the evaporation losses resulting from the spill in lb.
Q_R	=	the evaporation rate in lb/min.
t_{spill}	=	the time that the spill is on the ground in hours.

Therefore:

Q_R	=	represents the evaporation rate in lb/min.
u	=	8.94 m/sec
A_{spill}	=	1,000 ft^2
VP_{mdi}	=	1.733 x 10^{-5} mm Hg.
T_{spill}	=	302.6 °K.
M_W	=	250.26
K_{MDI}	=	0.56.

Substituting the values into the equation:

Q_R = **2.413×10^{-5} lb./min**

Therefore:

$L_{spill} = Q_R * t_{spill} * (60)$

Where:

t_{spill} = 20 hours

$L_{spill} = 2.896 \times 10^{-2}$ lb./year

8. Summary: Total Emissions

The total estimated MDI Emissions are:

Step No.	Process	MDI Emissions (lbs./year)
1	Storage	3.264×10^{-4}
2	Fugitive (Measured)	$5.633 \times 10^{+1}$
3	Fugitive (Equipment Leaks)	8.987×10^{-1}
4	Process (Cavity)	2.031×10^{-3}
5	Process (Foam Density)	9.759×10^{-3}
6	Process (Continuous)	1.225×10^{-1}
7	Process (Filling)	5.314×10^{-5}
8	Process (Adhesive)	4.99×10^{-1}
9	Process (Spray Coating)	4.94×10^{0}
10	Spill	2.896×10^{-2}
	Total	$6.283 \times 10^{+1}$

The total estimated emissions for the year is 62.83 lbs.

Appendix A – Vapor Pressure/Temperature Chart

MDI Vapor Pressure/Temperature Chart[3]

Table I: MDI Vapor Pressure Chart is a table that lists the Vapor Pressure of 4,4′-MDI vapor pressure (VP) at temperature from 20 ^{O}C to 207 ^{O}C.

To determine the vapor pressure of 4,4′-MDI at a temperature not listed or if the temperature range is outside the range of values listed, you may use the following equation:

Log (MDI VP in mm mercury) = 11.15 - 4809.8 / Temperature in ^{O}K

Where:

Temp in ^{O}K = 273 + Temp in ^{O}C

Temp in ^{O}C = 5/9 x (temp in ^{O}F – 32)

Table I: MDI Vapor Pressure Chart

Temperature (˚Farenheit)	Temperature (˚Celsius)	Vapor Pressure (mm Hg)
68.0	20	5.424E-06
69.8	21	6.168E-06
71.6	22	7.008E-06
73.4	23	7.956E-06
75.2	24	9.024E-06
77.0	25	1.023E-05
78.8	26	1.158E-05
80.6	27	1.310E-05
82.4	28	1.481E-05
84.2	29	1.673E-05
86.0	30	1.888E-05
87.8	31	2.130E-05
89.6	32	2.400E-05
91.4	33	2.702E-05
93.2	34	3.040E-05
95.0	35	3.418E-05
96.8	36	3.840E-05
98.6	37	4.310E-05
100.4	38	4.835E-05
102.2	39	5.420E-05
104.0	40	6.071E-05
105.8	41	6.795E-05
107.6	42	7.600E-05
109.4	43	8.494E-05
111.2	44	9.487E-05
113.0	45	1.06E-04

Temperature (˚Farenheit)	Temperature (˚Celsius)	Vapor Pressure (mm Hg)
152.6	67	1.008E-03
154.4	68	1.109E-03
156.2	69	1.220E-03
158.0	70	1.340E-03
159.8	71	1.472E-03
161.6	72	1.616E-03
163.4	73	1.774E-03
165.2	74	1.945E-03
167.0	75	2.132E-03
168.8	76	2.335E-03
170.6	77	2.557E-03
172.4	78	2.798E-03
174.2	79	3.061E-03
176.0	80	3.346E-03
177.8	81	3.656E-03
179.6	82	3.993E-03
181.4	83	4.358E-03
183.2	84	4.755E-03
185.0	85	5.186E-03
186.8	86	5.652E-03
188.6	87	6.158E-03
190.4	88	6.706E-03
192.2	89	7.299E-03
194.0	90	7.941E-03
195.8	91	8.635E-03
197.6	92	9.386E-03

3 Chakrabarti, A., *Vapor Pressure of Diphenylmethane Diisocyanate (MDI) Formulations*, The Dow Chemical Company, Midland, Michigan.

Temperature (˚Farenheit)	Temperature (˚Celsius)	Vapor Pressure (mm Hg)
114.8	46	1.181E-04
116.6	47	1.316E-04
118.4	48	1.466E-04
120.2	49	1.632E-04
122.0	50	1.815E-04
123.8	51	2.018E-04
125.6	52	2.242E-04
127.4	53	2.489E-04
129.2	54	2.761E-04
131.0	55	3.062E-04
132.8	56	3.393E-04
134.6	57	3.757E-04
136.4	58	4.158E-04
138.2	59	4.599E-04
140.0	60	5.083E-04
141.8	61	5.616E-04
143.6	62	6.200E-04
145.4	63	6.841E-04
147.2	64	7.544E-04
149.0	65	8.314E-04
150.8	66	9.158E-04
237.2	114	5.267E-02
239.0	115	5.670E-02
240.8	116	1.168E+00
242.6	117	1.239E+00
244.4	118	1.313E+00
246.2	119	1.392E+00
248.0	120	1.475E+00
249.8	121	1.562E+00
251.6	122	1.654E+00
253.4	123	1.752E+00
255.2	124	1.854E+00
257.0	125	1.962E+00
258.8	126	2.075E+00
260.6	127	2.195E+00
262.4	128	2.321E+00
264.2	129	2.454E+00
266.0	130	2.593E+00
267.8	131	2.740E+00
269.6	132	2.894E+00
271.4	133	3.057E+00
273.2	134	3.227E+00
275.0	135	3.407E+00
276.8	136	3.595E+00
278.6	137	3.793E+00
280.4	138	4.001E+00
282.2	139	4.220E+00
284.0	140	4.449E+00
285.8	141	4.690E+00
287.6	142	4.942E+00
289.4	143	5.207E+00
291.2	144	5.485E+00

Temperature (˚Farenheit)	Temperature (˚Celsius)	Vapor Pressure (mm Hg)
199.4	93	1.020E-02
201.2	94	1.107E-02
203.0	95	1.202E-02
204.8	96	1.304E-02
206.6	97	1.414E-02
208.4	98	1.533E-02
210.2	99	1.661E-02
212.0	100	1.799E-02
213.8	101	1.948E-02
215.6	102	2.108E-02
217.4	103	2.280E-02
219.2	104	2.466E-02
221.0	105	2.665E-02
222.8	106	2.879E-02
224.6	107	3.109E-02
226.4	108	3.356E-02
228.2	109	3.622E-02
230.0	110	3.906E-02
231.8	111	4.212E-02
233.6	112	4.540E-02
235.4	113	4.891E-02
321.8	16er1	1.168E+00
323.6	162	1.239E+00
325.4	163	1.313E+00
327.2	164	1.392E+00
329.0	165	1.475E+00
330.8	166	1.562E+00
332.6	167	1.654E+00
334.4	168	1.752E+00
336.2	169	1.854E+00
338.0	170	1.962E+00
339.8	171	2.075E+00
341.6	172	2.195E+00
343.4	173	2.321E+00
345.2	174	2.454E+00
347.0	175	2.593E+00
348.8	176	2.740E+00
350.6	177	2.894E+00
352.4	178	3.057E+00
354.2	179	3.227E+00
356.0	180	3.407E+00
357.8	181	3.595E+00
359.6	182	3.793E+00
361.4	183	4.001E+00
363.2	184	4.220E+00
365.0	185	4.449E+00
366.8	186	4.690E+00
368.6	187	4.942E+00
370.4	188	5.207E+00
372.2	189	5.485E+00
374.0	190	5.776E+00
375.8	191	6.082E+00

293.0	145	5.776E+00
Temperature (˚Farenheit)	Temperature (˚Celsius)	Vapor Pressure (mm Hg)
294.8	146	6.082E+00
296.6	147	6.402E+00
298.4	148	6.738E+00
300.2	149	7.090E+00
302.0	150	7.458E+00
303.8	151	7.844E+00
305.6	152	8.249E+00
307.4	153	8.672E+00
309.2	154	9.115E+00
311.0	155	9.578E+00
312.8	156	1.006E+01
314.6	157	1.057E+01
316.4	158	1.110E+01
318.2	159	1.166E+01
320.0	160	1.224E+01

377.6	192	6.402E+00
Temperature (˚Farenheit)	Temperature (˚Celsius)	Vapor Pressure (mm Hg)
379.4	193	6.738E+00
381.2	194	7.090E+00
383.0	195	7.458E+00
384.8	196	7.844E+00
386.6	197	8.249E+00
388.4	198	8.672E+00
390.2	199	9.115E+00
392.0	200	9.578E+00
393.8	201	1.006E+01
395.6	202	1.057E+01
397.4	203	1.110E+01
399.2	204	1.166E+01
401.0	205	1.224E+01
402.8	206	1.284E+01
404.6	207	1.348E+01

Appendix B – Vapor Pressure of MDI/PMDI Mixtures

Table II: MDI/PMDI Adjustment Factors Chart

PMDI is considerably less volatile than MDI and as a consequence mixtures of MDI/PMDI have a lower vapor pressure than pure MDI. Engineering estimates that are based on the vapor pressure of pure MDI may significantly overestimate the reportable emissions of a facility, therefore, an adjustment factor will have to be used. The adjustment factors are a ratio of the ratio of the vapor pressure of MDI/PMDI mixtures and the vapor pressure of pure MDI. Your release estimates, calculated assuming pure MDI, should be corrected for the presence of PMDI by multiplying your estimates by the appropriate factor. The table in this appendix shows the adjustment factor as it relates to the percent MDI in the mixture at a specific temperature.

Table II: MDI/PMDI Adjustment Factors Chart

				Percentage MDI							
Temperature											
Fahrenheit	0	10	20	30	40	50	60	70	80	90	100
70	0.09	0.18	0.27	0.37	0.45	0.54	0.64	0.73	0.83	0.92	1.00
80	0.11	0.20	0.29	0.38	0.46	0.55	0.65	0.74	0.83	0.92	1.00
90	0.12	0.21	0.30	0.39	0.47	0.65	0.65	0.74	0.83	0.92	1.00
100	0.13	0.22	0.31	0,40	0.48	0.57	0.66	0.74	0.84	0.92	1.00
110	0.14	0.23	0.33	0.41	0.49	0.58	0.66	0.75	0.84	0.92	1.00
120	0.16	0.24	0.35	0.41	0.50	0.58	0.67	0.75	0.84	0.93	1.00
130	0.17	0.25	0.35	0.42	0.50	0.59	0.67	0.71	0.84	0.93	1.00
140	0.18	0.26	0.36	0.43	0.51	0.60	0.68	0.76	0.85	0.93	1.00
150	0.20	0.27	0.37	0.44	0.51	0.61	0.68	0.76	0.85	0.93	1.00
160	0.21	0.28	0.37	0.45	0.52	0.61	0.69	0.76	0.85	0.93	1.00
170	0.22	0.29	0.38	0.46	0.53	0.62	0.69	0.77	0.85	0.93	1.00
180	0.24	0.31	0.39	0.47	0.54	0.62	0.70	0.77	0.85	0.93	1.00
190	0.25	0.33	0.40	0.47	0.55	0.63	0.70	0.77	0.86	0.93	1.00
200	0.27	0.34	0.42	0.48	0.55	0.63	0.71	0.78	0.86	0.93	1.00
210	0.29	0.36	0.44	0.51	0.57	0.65	0.72	0.79	0.86	0.93	1.00
230	0.31	0.40	0.48	0.54	0.60	0.69	0.72	0.79	0.86	0.94	1.00
248	0.33	0.44	0.52	0.58	0.65	0.70	0.74	0.80	0.86	0.94	1.00
266	0.37	0.46	0.58	0.63	0.69	0.73	0.75	0.80	0.86	0.94	1.00
284	0.41	0.49	0.66	0.68	0.72	0.76	0.79	0.82	0.88	0.94	1.00
302	0.43	0.50	0.70	0.74	0.77	0.78	0.80	0.82	0.88	0.95	1.00
320	0.48	0.52	0.74	0.77	0.79	0.80	0.82	0.84	0.9	0.95	1.00
360	0.55	0.59	0.78	0.80	0.82	0.84	0.86	0.88	0.91	0.95	1.00
400	0.63	0.68	0.80	0.82	0.84	0.86	0.88	0.90	0.92	0.96	1.00
450	0.75	0.80	0.82	0.84	0.86	0.88	0.90	0.92	0.93	0.96	1.00
480	0.82	0.83	0.85	0.87	0.89	0.91	0.93	0.95	0.96	0.97	1.00

Appendix C - Breathing Losses From Storage Tanks

The objective of this analysis is to present a simplified method to estimate breathing losses from fixed roof storage tanks and compare the estimated losses with results obtained from the conventional EPA methodology.

1. Description of simplified procedure

Breathing losses occur because differences in temperature (such as changes between day and night temperatures) affect the vapor space pressure inside storage tanks. Vapors expand with an increase in temperature and contract with a decrease in temperature. In addition, the saturated vapor concentration of a substance in air increases with an increasing temperature and decreases with a decreasing temperature. As the outside temperature rises during the day, the pressure inside a tank increases and air will be expelled from the tank. As the temperature falls during the night, pressure in the tank decreases and fresh airflows into the tank.

The method used to calculate the breathing losses is an adaptation of an EPA method published in AP-42 (Supplement E of AP-42 – October 1992).

Consider a tank with a volume of V_T (gallons). Assume that the liquid level in the tank is L_T. The vapor space V_v (gallons) of the tank is:

$$V_v = V_T \times (100-L_T) / 100$$

Assume that the average ambient temperature is T_{amb} (in °K). Assume also that the day-night temperature fluctuation is T_R (in °K).

The vapor expansion factor K_E due to day-night temperature fluctuation is defined as:

$$K_E = T_R / T_{amb}$$

The total air displaced per day (M_{air} in lbmole/day) is calculated from the following expression:

$$M_{air} = (V_v / 7.48) \times (1 / 359) \times K_E \times (273.15 / T_{amb})$$

The breathing losses can now be estimated from the following expression:

$$L_b = 365 \times M_{air} \times (VP_{amb} / 760) \times M_w \times K_{mdi}$$

Where:

L_b	=	Breathing losses in lb/year
M_{air}	=	Total air displaced per day in lb-mole/day
VP_{amb}	=	Vapor pressure of MDI at the ambient temperature in mm Hg
M_w	=	Molecular weight of MDI 250.26)
K_{mdi}	=	Adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature
365	=	days/year
359	**=**	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

2. Conventional EPA methodology

a. Old EPA method

The original method to estimate breathing losses was first proposed in July 1962 by the American Petroleum Institute. The methodology was reaffirmed in August 1987 in API Bulletin 2518. EPA adopted the method and incorporated it in Appendix C of AP-42 (4^{th} Edition, September 1985)

The empirical equation presented in AP-42 is applicable to tanks with vertical cylindrical shells and fixed roofs. The tanks must be substantially liquid and vapor tight and must operate approximately at atmospheric pressure. Under these conditions, breathing losses can be estimated from:

$$L_B = 2.26 \times 10^{-2} \times M_v (P/P_A-P)^{0.68} \times D^{1.73} \times H^{0.51} \times \Delta T^{0.50} F_P \times C \times K_c$$

Where:

L_B	=	Fixed roof breathing loss in lbs./yr.
M_v	=	Molecular weight of vapor in storage.
P_A	=	Average atmospheric pressure at tank location in psia
P	=	Vapor pressure of compound at bulk liquid conditions in psia
D	=	Tank Diameter in ft
H	=	Average vapor space height, including roof volume correction in ft
ΔT	=	Average ambient diurnal temperature change in ^oF
F_P	=	Paint factor
C	=	Adjustment factor for small diameter tanks
K_c	=	Product factor. For crude oil $K_c = 0.65$. For all other organic liquids $K_c = 1.0$.

b. New EPA method

The EPA adopted a new method to estimate breathing losses (often referred to as standing loss) from storage tanks and incorporated it in Supplement E of AP-42 (October 1992).
The new method is applicable to vertical tanks and can be used to estimate breathing losses from tanks equipped with a conservation vent. The method can also be adapted to estimate breathing losses from horizontal tanks.

The operating equation is given below:

$$L_s = 365 \times V_v \times W_v \times K_E \times K_s$$

Where:

L_s	=	Standing storage loss in lbs.yr
V_v	=	Vapor space volume in ft^3
W_v	=	Vapor density in $lbs.ft^3$
K_E	=	Vapor space expansion factor, dimensionless
K_s	=	Vented vapor saturation factor, dimensionless
365	=	days/year

The EPA publication provides detailed guidelines for evaluating each of the above terms.

- The vapor space volume (V_v) is the vapor space above the liquid. For a cylindrical tank, V_v is equal to the cross sectional area of the tank times the tank outage. Specific instructions are given to evaluate the vapor space volume for vertical tanks equipped with a dome or a cone and for horizontal tanks.

- The vapor density of the vapor (W_v) is calculated from the molecular weight of the liquid (M_v), the daily average liquid surface liquid temperature (T_{LA}) and the vapor pressure of the liquid (P_{vA}) at the daily average liquid surface temperature using the ideal gas equation. The daily average liquid surface temperature (T_{LA}) is a function of the daily ambient temperature ambient (ΔT_{AA}), the liquid bulk temperature (T_B), the tank paint absorptance (α) and the total daily insulation factor (I).

- The vapor space expansion factor (K_E) is determined from the increase in volume due to the change in the daily vapor temperature and the change in vapor pressure of the liquid at the liquid surface temperature. Specific instructions are given to determine the vapor space expansion factor. The daily vapor temperature range (ΔT_v) is a function of the daily average ambient temperature (ΔT_A), the tank paint absorptance (α) and the total daily insulation factor (I).

- The vented vapor saturation factor (K_s) can be viewed as the approach to saturation of the liquid in the vapor space. I t is a function of the vapor pressure at the daily average liquid temperature and tank outage. The saturation factor approaches 1.0 when the vapor pressure is low or the tank outage is small.

As noted above the new EPA method recognizes that the temperature of the liquid and the temperature of the vapor space may be different from the ambient temperature. Empirical formulas are provided to determine the required temperatures if the ambient temperature and the daily range are given.

Determination of the breathing losses through the new EPA method is quite tedious. A software program to evaluate storage tank losses (working losses and breathing losses) was developed by the EPA. The software (Tanks 4.0) is available for downloading from the EPA home page on the Internet.

3. Comparison of results

The simplified method used for the MDI Emissions Estimator is an adaptation of the new EPA method. In developing the simplified method the following assumptions are made:

- The pressure term in the vapor space expansion factor is ignored. It can be shown that for liquids having a low vapor pressure the pressure term is negligible relative to the temperature term and can thus be ignored.
- The vented vapor saturation factor is 1.0. It can be shown that for liquids having a low vapor pressure the vented vapor saturation factor approaches 1.0.
- The average liquid surface temperature and the vapor temperature are the same as the ambient temperature.

Under these circumstances, the simplified method will yield identical results to the new EPA method.

Table 1 provides a side-by-side comparison of the working losses and breathing losses for the three methods discussed above.

COMPARATIVE EXAMPLE

The following illustrative example demonstrates the equivalency between the simplified method and the new EPA method when simplifying assumptions are made:

A fixed roof vertical tank contains MDI. The tank has a volume of 11,750 gallons (10’ D x 20” H) and is half full. The tank is located in New York. From meteorological data, the daily average ambient temperature is 54.55 ^{o}F (12.53 ^{o}C) and the daily average temperature range is 15.3 ^{o}F (8.5 ^{o}C). The MDI vapor pressure at the daily average temperature is 1.945×10^{-6} mm Hg.

Simplified method

V_v = 11,750 x 0.5 = 5,875 gallons

K_E = 8.5 / (12.53 + 273.15) = 0.02975

M_{air} = 5,875 / 7.48) x (1 / 359) x 0.02975 x (273.15 / 285.68) = 0.06229 lb-mole/day

L_b = 365 x 0.06229 x (1.945 x 10^{-6}) / 760) x 254.38

L_b = 1.480 x 10^{-5} lbs.yr

1. New EPA method using simplifying assumptions

The operating equation is given below:

L_s = 365 x V_v x W_v x K_E x K_s

V_v = 5,875 / 7.48 = 785.40 ft^3

W_v = $\frac{254.38 \text{ x } (1.945 \text{ x } 10^{-6} \text{ } 14.7 / 760)}{10.73 \text{ x } (54.55 + 460)}$ = **1.733 x 10^{-9} lbs.ft^3**

K_E = 15.3 / (54.55 +460) = 0.02973

K_s = 1.0

L_s = 365 x 785.40 x 1.733 x 10^{-9} x 0.02973 x 1.0

L_s = 1.474 x 10^{-5} lbs.yr

2. New EPA method without simplifying assumptions

The operating equation is given below:

L_s = 365 x V_v x W_v x K_E x K_s

V_v = 5,875 / 7.48 = 785.40 ft^3

W_v = $\frac{254.38 \text{ x } (2.194 \text{ x } 10^{-6} \text{ } 14.7 / 760)}{10.73 \text{ x } (56.13 + 460)}$ = **1.949 x 10^{-9} lbs.ft^3**

K_E = 0.03214 (from Table 1)

K_s = 1.0 (from Table 1)

L_s = 365 x 785.40 x 1.949 x 10^{-9} x 0.03214 x 1.0

L_s = 1.796 x 10^{-5} lbs.yr

TABLE 1
MDI LOSSES FROM STORAGE TANKS
Comparison of results with EPA methods

Tank No.	T-501		**Tank type**	Vertical fixed roof		Date		3/15/00	
Material stored	MDI		**Company**	National Coatings		Performed by		Dennis Miller	
City	New York		**State**	NY					
Description	Outdoor storage tank								
	INPUT DATA					**CALCULATIONS**			
		Symbol		**Units**			**Symbol**		**Units**
Vapor pressure Antoine constants					**New EPA method (AP-42) ***				
Constant A			10.902						
Constant B			4634.09		**Breathing losses**				
Constant C			266.415		Tank vapor space volume		Vv	785.4	ft3
Molecular weight		Mv	254.38	Lb/lb-mole	Vapor density		Wv	1.949E-09	lb/ft3
					Vapor space expansion factor		KE	3.214E-02	
Tank design data					Vented vapor saturation factor		Ks	1.000E+00	ft2
Shell height		Hs	20	ft					
Diameter		D	10	ft	Breathing losses		LB	1.796E-05	lb/yr
Liquid height			20	ft					
Avg. Liquid height		HL	10	ft	Working losses		Lw	3.020E-05	lb/yr
Tank volume			11749.584	gallons					
Tutrnovers		N	10		**Total losses**		LT	4.815E-05	lb/yr
Net throughput		Q	117495.84	gallons/yr					
Meteorological data					**Simplified method ****				
Daily ave. ambient temp.		TAA	54.55	°F					
Daily max. ambient temp.		TAX	62.2	°F	Breathing losses				
Daily min. ambient temp.		TAN	46.9	°F	Temperature expansion factor			2.977E-02	
Daily ambient temp. range		DTA	15.3	°F	Air displaced per day			6.227E-02	lbmole/day
Tank paint solar absorptance		a	0.17						
Daily total insolation factor		I	1171	Btu/ft2-day	Breathing losses		LB	1.480E-05	lb/yr
Liquid bulk temperature		TB	54.57	°F	Working losses		Lw	2.724E-05	lb/yr
Daily vapor temp. range		DTv	16.58996	°F					
					Total losses		LT	4.203E-05	lb/yr
Daily ave. liquid surface temp.		TLA	56.133853	°F					
Daily max. liquid surface temp.		TLX	60.281343	°F					
Daily min. liquid surface temp.		TlN	51.986363	°F	**Old EPA method *****				
VP @ daily ave. liquid surf. temp.		PvA	2.194E-06	mm Hg	Breathing losses *		LB	5.336E-03	lb/yr
VP @ daily max. liquid surf. temp.		PvX	2.995E-06	mm Hg					
VP @ daily min. liquid surf. temp.		PvN	1.598E-06	mm Hg	Working losses		Lw	3.020E-05	lb/yr
VP @ daily ave. ambient temp.		Pamb	1.945E-06	mm Hg	**Total losses**		LT	0.005366	lb/yr
Daily vapor pressure range		DPv	1.397E-06	mm Hg					
Breather vent pressure setting range			0	psia	For old EPA method				
Breather vent pressure setting range		DPB	0	mm Hg	Paint factor (white - good condition)		Fp	1	
					Adjustment for small diameter tanks		C	0.95	

***** **New EPA metho(Source AP-42 - Supplement E - October 1992)**
LS = 365 *Vv * Wv * Ke * Ks

****** **Simplified method (Adaptation of the new EPA method)**

******* **Old EPA metho (Source AP-42 - Appendix C - September 1985)**
LB = 0.0226 * MV * ((Pamb/(760-Pamb))^0.68 * D^1.73 *(Hs-HL)^0.51*(DTA)^0.50 * Fp * C

Appendix D – Basic Formulas

The following are the basic formulas used to calculate the emissions for the various applications.

1.0 Calculating Working Losses from Storage Tanks

Working losses occur when MDI/PMDI vapor that is present over the liquid in a storage tank is displaced from the tank by the addition of MDI/PMDI liquid during tank filling. A reasonable worst case estimate of working losses can be made based on the size and number of storage tanks, the average storage temperature, and the number of times each tank is filled in one year.

The working losses can be estimated from the following expression:

$$L_w = Q_w * (1 / 359) * (273.15 / T_{amb}) * (VP_{amb} / 760) * M_w * K_{mdi}$$

Where:

L_w	=	the working losses in lb/year.
Q_w	=	the annual throughput of MDI pumped to the tank in ft^3/year.
T_{amb}	=	the ambient temperature in °K.
VP_{amb}	=	the vapor pressure of MDI at the ambient temperature in mm Hg.
M_w	=	the molecular weight of MDI (250.26).
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

2.0 Calculating Breathing Losses from Storage Tanks

Breathing losses occur because differences in temperature (such as changes between day and night temperatures) affect the vapor space pressure inside storage tanks. Vapors expand with an increase in temperature and contract with a decrease in temperature. In addition, the saturated vapor concentration of a substance in air increases with increasing temperature and decreases with a decreasing temperature. As outside temperature rises during the day, pressure inside a tank increases and air will be expelled from the tank. As the temperature falls during the night, pressure in the tank decreases and fresh air flows into the tank.

The method used to calculate the breathing losses is an adaptation of an EPA method published in AP-42. The breathing losses can be calculated from the following expression:

$$L_b = 365 * M_{air} * (VP_{amb} / 760) * M_w * K_{mdi}$$

$$M_{air} = (V_v / 7.48) * (1 / 359) * K_E * (273.15 / T_{amb})$$

$$V_v = V_T * (100\text{-}L_T)$$

$$K_E = T_R / T_{amb}$$

Where:

L_b	=	the breathing losses in lb/year.
M_{air}	=	the total air displaced per day in lb-mole/day.

VP_{amb} = the vapor pressure of MDI at the ambient temperature in mm Hg

M_w = the molecular weight of MDI (250.26).

K_{mdi} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

T_{amb} = the average ambient temperature in °K.

T_R = the average day-night temperature fluctuation in °K.

K_E = the vapor expansion factor due to day-night temperature fluctuation.

3.0 Calculating Fugitive Emissions from Process Areas

Fugitive emissions are air releases of volatile chemicals that typically occur due to leaks from fittings and seals in chemical process equipment, transfer operations or storage systems. Direct measurement or monitoring data can be used to estimate fugitive emissions whenever possible. In the absence of direct measurement or monitoring data, industrial hygiene data on MDI concentrations in the workplace can be used to estimate MDI or MDI/PMDI fugitive emissions. This technique can only be used if the industrial hygiene data are representative of average concentrations throughout the year and throughout the building.

The fugitive emissions can be estimated from the following expression:

$$L_{fg} = C_{mdi} * (V_B / 359) * N_{year} * (273.15 / T_{amb}) * M_w * K_f$$

Where:

L_{fg} = the fugitive emissions in lb/year.

C_{mdi} = the average MDI concentration, in ppmv, in the air within the building.

V_B = the volume of the workspace building in ft^3.

N_{year} = the number of air exchanges per year.

T_{amb} = the ambient temperature in °K.

M_w = the molecular weight of MDI (250.26).

K_f = the adjustment factor to the MDI concentration in the building air. A value of 1.10 is used.

359 = **the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.**

4.0 Calculating Fugitive Emissions from Equipment Leaks

In cases where monitoring data is not available, EPA has developed a method using emission factors based upon the type of fittings and number of fittings used in the process. The methodology used for MDI/PMDI is an adaptation of an EPA Correlation Method ("1995 Protocol for Equipment Leak Emission Estimate" - EPA-453/R-95-017). The method presented here uses the actual formulas recommended by the EPA except that saturated vapor concentrations are used instead of screening values. Since the vapor concentration of MDI cannot exceed the saturation vapor pressure at a given temperature, the predicted screening values are limiting and conservative values. The calculation methodology involves the following steps:

1. Determine the saturated concentration of MDI.
2. Calculate emission factor for each equipment type.
3. Determine emissions for each equipment type.
4. Determine total losses from equipment leaks.

The MDI emissions from equipment leaks using the Modified Correlation Approach can be determined using the following equations:

$$SV = 1{,}315.8 \times 10^{[(10.902 - 4634.09/(266.15 + t)]}$$

Where:

SV = Screening Value in ppmv and

t = Temperature in ^{o}C.

The calculated Screening Value (SV) is then inserted into the Leak Rate/Screening Value Correlation Formula for the appropriate equipment type (found in Table V-6) and the leakage rate is determined.

Table V-6
Leak Rate/Screening Value Correlations

Equipment Type	Correlation Leak Rate (kg/hr) $(a*(SV)^{b})$
Gas Valve	$1.87x10^{-06} \times (SV)^{0.873}$
Light Liquid Valve	$6.41x10^{-06} \times (SV)^{0.787}$
Light Liquid Pump [c]	$1.90x10^{-05} \times (SV)^{0.824}$
Connectors	$3.05x10^{-06} \times (SV)^{0.885}$

[c] **This equation can be used for liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pumps**

The total emissions from equipment leaks will be equal to the emissions contributed from each gas valves, light liquid valves, light liquid pumps, and connectors.

The emissions factors can be estimated from the following expressions:

For gas valves:

$$K_{gas} = 1.87 \times 10^{-6} * (C_{mdi})^{0.873}$$

For liquid valves:

$$K_{liq} = 6.41 \times 10^{-6} * (C_{mdi})^{0.787}$$

For liquid pumps, compressor seals, pressure relief valves, agitator seals and heavy liquid pumps:

$$K_{pump} = 1.90 \times 10^{-5} * (C_{mdi})^{0.824}$$

For connectors:

$$K_{con} = 3.05 \times 10^{-6} * (C_{mdi})^{0.885}$$

Where:

K_{gas} = the emission factor for gas valves in kg/year-item.

K_{liq} = the emission factor for liquid valves in kg/year-item.
K_{pump} = the emission factor for liquid pumps in kg/year-item.
K_{con} = the emission factor for connectors in kg/year-item.

For Gas Valves the emissions can then be estimated from the following expression:

$$L_{gv} = K_{gas} * n_{gv} * K_{mdi} * t_{pr}$$

L_{gv} = the annual losses from liquid valves in lb/yr.
n_{gv} = the number of liquid valves.
K_{mdi} = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
t_{pr} = the total time in hours/year that the process is operating.

For Liquid Valves the emissions can then be estimated from the following expression:

$$L_{liq} = K_{liq} * n_{liq} * K_{mdi} * t_{pr}$$

L_{liq} = the annual losses from liquid valves in lb/yr.
n_{liq} = the number of liquid valves.
K_{mdi} = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
t_{pr} = the total time in hours/year that the process is operating

For liquid Pumps the emissions can then be estimated from the following expression:

$$L_{pump} = K_{pump} * n_{pump} * K_{mdi} * t_{pr}$$

L_{pump} = the annual losses from liquid valves in lb/yr.
n_{pump} = the number of liquid valves.
K_{mdi} = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
t_{pr} = the total time in hours/year that the process is operating

For Connectors the emissions can then be estimated from the following expression:

$$L_{con} = K_{con} * n_{con} * K_{mdi} * t_{pr}$$

L_{con} = the annual losses from liquid valves in lb/yr.
n_{con} = the number of liquid valves.
K_{mdi} = adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
t_{pr} = the total time in hours/year that the process is operating

Total Emissions can then be estimated from the following expression:

$$E_{tot} = L_{gas} * L_{liq} * L_{pump} * L_{con}$$

5.0 Calculating Emissions from Enclosed Processes (Based on Cavity Size)

To estimate emissions from enclosed processes when the volume of the mold is known or can be determined. The emissions from the process will correspond to the total volume of air displaced from the molding operations at the temperature of the process. A reasonable worst case estimate of emissions can be made based on the volume of the mold cavity, the number of pieces produced per year and the maximum process temperature.

The enclosed process losses can be estimated from the following expression:

$$L_c = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * M_w * K_{mdi}$$

Where:

L_c	=	the emissions from the enclosed process in lb/year.
V_{air}	=	the annual volume of displaced air in ft^3/year.
T_{proc}	=	the process temperature in °K. This is the maximum temperature of the MDI "tack free" time.
VP_{mdi}	=	the vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

6.0 Calculating Emissions from Enclosed Processes (Based on Foam Density)

To estimate emissions from enclosed processes when the volume of the mold is not known or when a large number of different cavity or mold sizes are filled each year. For this situation the emissions can be estimated from:

1. The density of the cured foam
2. The total weight of the MDI-based component in the foam
3. The Temperature of the foam at the "tack free" or "string" time during the curing process.

The enclosed process losses can be estimated from the following expression:

$$L_{fd} = V_{air} * (1 / 359) * (273.15 / T_{proc}) * (VP_{mdi} / 760) * M_w * K_{mdi}$$

Where

L_{fd}	=	the emissions from the enclosed process in lb/year.
V_{air}	=	the annual volume of displaced air in ft3/year.
T_{proc}	=	the process temperature in °K. This is the maximum temperature of the MDI "tack free" time.
VP_{mdi}	=	the vapor pressure of MDI in mm Hg. at process temperature.
M_w	=	250.26 (this is the molecular weight of MDI).
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

7.0 Calculating Emissions from Open Processes (Continuous Processes)

To estimate emissions from open processes such as boardstock production. For this situation it is assumed that MDI will migrate from all exposed surfaces. The evaporation losses are a function of the process temperature, the airflow speed in the vicinity of the process, the "tack-free" time and the exposed surface area.

The calculation methodology involves four steps:

1.Determine partial pressure of MDI at "tack-free" time.
2. Determine exposed area.
3. Determine evaporation rate.
4. Apply adjustment factor.

The evaporation rate (in gr/day) is determined from the following expression:

$$W = 25.4 * VP_{mdi} * (M_w / T_{proc}) * (u^{0.78}) * SA * t_{TF} * K_{mdi}$$

Where

W	=	the evaporation losses from the open process in **gr/day**.
VP_{mdi}	=	the vapor pressure of MDI in atm. at process temperature.
T_{proc}	=	the process temperature in °K. This is the maximum temperature of the MDI "tack free" time.
M_w	=	250.26 (this is the molecular weight of MDI).
u	=	the air flow speed in m/sec. This is the air flow in the vicinity of the process.
SA	=	the exposed surface area in M^2. This is the exposed surface area per day. For boardstock production, the surface area can be determined from the dimensions of the board.
t_{TF}	=	the "tack-free" time in seconds. The default value is 5 sec.
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The open process losses are determined by multiplying the evaporation losses per day by the number of days the process is in operation.

8.0 Calculating Emissions from Mixing/Blending/Filling Process

Calculating Stack Emissions

Estimating emissions from a mixing/blending operation will correspond to the total volume of air displaced from the containers at the filling temperature. The reasonable worst case scenario will be to assume that the volume of air displaced from the container is saturated with MDI/PMDI. Loses will be experienced when the reactor or blend tank is filled with the MDI/PMDI mixture and when the reactor/blend tank is emptied into containers. Loses will be based upon the volume of MDI/PMDI charged to the reactor/blend tank and the volume of containers filled with the blend.

The filling losses can be estimated from the following equation:

$$L_{fll} = V_{air} * (1 / 359) * (273.15 / T_{fill}) * (VP_{MDI} / 760) * M_w * K_{MDI} * C_{blnd}$$

Where:

L_{fll} = the emissions from the filling operation in lbs/year

V_{air} = the annual volume of displaced air in ft^3/year

T_{fill} = the temperature the material is charged or filled at in ^oK

VP_{MDI} = the vapor pressure of MDI in mm Hg at the charging/filling temperature.

M_W = the molecular weight of MDI (250.26)

K_{MDI} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and/or blend and at the blending/filling temperature.

C_{blnd} = the proportion of MDI/PMDI in the blend. If only MDI/PMDI is filled then C_{blnd} is 1.

9.0 Calculating Emissions from a Spray Booth Operation

The emissions associated with a spray booth operation will be governed by the exhaust air flow rate and the temperature at which the spray coating is carried out. If the concentration of the exit gas is not known , the worst-case scenario is to assume that the air is saturated with MDI/PMDI at the exit temperature.

The emissions from spray coating operations can be estimated from the following expression:

$$L_{sp} = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * t_{sp}$$

Where:

L_{sp} = the emissions in lb/year for spray coating operations.

V_{air} = the exhaust air flow rate in ft3/min.

T_{sp} = the spray temperature in °K.

C_{mdi} = the MDI concentration, in ppmv, in the exhaust air.

M_W = the molecular weight of MDI (250.26).

K_{MDI} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

t_{sp} = the total time in hours/year that spray coating is occurring.

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

C_{mdi} = $(VP_{MDI}/760) \times 10^6$

VP_{MDI} = MDI vapor pressure at exhaust temperature.

10.0 Spills:

A liquid chemical accidentally spilled onto the ground may spread out over an area, vaporize and cause an air emission. Such accidental releases must be reported under section 313. Evaporative losses from spills (and other open processes) depend on a number of factors including:

1. The volatility of the material
2. The size of the spill
3. The temperature of the surrounding area
4. The wind speed
5. The time that the liquid from the spill is allowed to evaporate

A fairly simple model proposed by the EPA that accounts for all these factors is provided by the following equation:

$$Q_R = (0.284/82.05) * (u)^{0.78)} * A_{spill} * (VP_{MDI}/T_{spill}) * (M_W)^{2/3} * K_{mdi}$$

Where:

Q_R	=	the evaporation rate in lb/min.
u	=	the air flow speed in m/sec. This is the air flow in the vicinity of the process.
A_{spill}	=	the area of the spilled material in ft^2
VP_{mdi}	=	the vapor pressure of MDI in mm Hg. at the spill temperature.
T_{spill}	=	the average evaporation temperature in °K.
M_W	=	the molecular weight of MDI (250.26).
K_{mdi}	=	the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

The spill losses can be determined by multiplying the evaporation rate (QR) in lb/min by the time the spill is on the ground and converting the calculated value to the desired units:

$$L_{spill} = Q_R * t_{spill} * (60)$$

Where:

L_{spill}	=	the evaporation losses resulting from the spill in lb.
Q_R	=	the evaporation rate in lb/min.
t_{spill}	=	the time that the spill is on the ground in hours.

11.0 Calculation Emissions from Continuous Process (Carpet & Rug Application).

The emissions from carpet coating operation can be estimated from the following expression:

$$L_{cc} = (V_{air}/359)\ (60)\ (ppmv/1000000)\ (MW)\ (K_{MDI})\ (C_{iso}/100)\ (t_{cc})\ (R_{MDI}) \quad (1)$$

Where:

L_{cc}	=	the emissions in lb/year for carpet coating operations.
V_{air}	=	the exhaust airflow rate in ft^3/min (at 32 ^oF = 0^oC).
ppmv	=	the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure.
T_{st}	=	the temperature of the air leaving the stack in °K.
W	=	the molecular weight of MDI (250.26).
K_{MDI}	=	adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of K_{MDI} is 1.00 for pure MDI.
C_{iso}	=	the % of isocyanate feedstock in the total formulation.
R_{MDI}	=	represents the unreacted fraction of MDI on the conveyor belt relative to the MDI initially present in the formulation. This value reflects the unreacted fraction of MDI present at the midpoint of the application process and is based upon a first-order reaction.

t_{cc}	=	the total time of operation in hours/year.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0^oC and 1-atmosphere.
60	=	time, minutes/hour.

A first order reaction can be expressed by the following reaction:

$$R_{mdi} = e^{-(k)\,(tR)}$$

Where:

R_{MDI}	=	the unreacted fraction of MDI
k	=	the first order reaction rate constant in min^{-1}
t_R	=	the reaction time in minutes

12. Foundry & Casters.

The emissions from the foundry/casters can be estimated using the following equations:

A. Core Box Step:

During this step the MDI formulation is injected into the mold at ambient temperature. The losses will correspond to the total volume of air displaced from the molds at the filling temperature. A reasonable worst-case estimate of filling losses can be made based on the total volume of MDI formulation consumed, the composition of the MDI formulation and the injection temperature.

The core box losses can be estimated from the following expression:

$$L_{cb} = V_{air} * (1 / 359) * (273.15 / T_{cb}) * (VP_{mdi} / 760) * MW * K_{mdi} * C_{iso}/100$$

Where:

L_{cb}	=	the emissions from the core box step in lb/year.
V_{air}	=	the annual volume of displaced air in ft^3/year (at the filling temperature).
T_{cb}	=	the filling temperature in °K.
VP_{mdi}	=	the vapor pressure of MDI in mm Hg. at the filling temperature..
MW	=	the molecular weight of MDI (250.26).
K_{mdi}	=	an adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature..
C_{iso}	=	the % of isocyanate feedstock in the total formulation. If only MDI/PMDI material is filled then C_{iso} = 100%.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

B. Mold Pour and Shakeout Step

During the ore pour and shakeout step, exhaust air blowers are used to maintain a slight negative pressure in the process area by continuously sucking air and exhausting it to the atmosphere through a series of exhaust stacks. Residual MDI is thus removed from the mold and the sand. For this situation the MDI emissions can be estimated by considering the air exhaust rate, the temperature of the exit gas, the residual free MDI in the mold, and the "effective" MDI concentration in the gas stream. As a worst-case scenario, it can be assumed that the air leaving the process area will be in thermodynamic equilibrium with the free MDI remaining in the mold.

The losses from the mold pour and shakeout step can be estimated from the following expression:

$$Lso = (V_{air}/359) * (60) * (ppmv/1000000) * (MW) * (K_{mdi}) * (C_{iso}/100) * (t_{so}) * (F_{mdi})$$

Where:

L_{so} = the emissions in lb/year from the shakeout and mold pour step.

V_{air} = the exhaust airflow rate in ft^3/min (at stack temperature).

ppmv = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure.

MW = the molecular weight of MDI (250.26).

K_{mdi} = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio In the isocyanate feedstock and the temperature. The value of K_{mdi} is 1.00 for pure MDI.

C_{iso} = the % of isocyanate feedstock in the total formulation.

F_{mdi} = the fraction of free MDI remaining in the mold. The free MDI is assumed to be 0.01

T_{so} = the total time of operation in hours/year.

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

60 = time, minutes/hour.

Mold Pour:

L_{mp} = the emissions in lb/year from the mold pour step.

V_{air} = the exhaust airflow rate in ft^3/min (at stack temperature).

ppmv = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure.

MW = the molecular weight of MDI (250.26).

K_{mdi} = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio in the isocyanate feedstock and the temperature. The value of K_{mdi} is 1.00 for pure MDI.

C_{iso} = the % of isocyanate feedstock in the total formulation.

F_{mdi} = the fraction of free MDI remaining in the mold.

T_{so} = the total time of operation in hours/year.

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

60 = time, minutes/hour.

Shakeout

L_{so} = the emissions in lb/year from the shakeout step.

V_{air} = the exhaust airflow rate in ft^3/min (at stack temperature).

ppmv = the saturated concentration of pure MDI in air (in ppmv) at the stack temperature (T_{st}). It is directly determined from the vapor pressure.

MW = the molecular weight of MDI (250.26).

K_{mdi} = adjustment factor to the vapor pressure that is a function of the MDI/PMDI ratio

In the isocyanate feedstock and the temperature. The value of K_{mdi} is 1.00 for pure MDI.

C_{iso}	=	the % of isocyanate feedstock in the total formulation.
F_{mdi}	=	the fraction of free MDI remaining in the mold.
T_{so}	=	the total time of operation in hours/year.
359	=	the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.
60	=	time, minutes/hour.

13. Oriented Strand Board (OSB)

Methylene*bis* (phenyl isocyanate) (MDI) is used as a binder in the production of particleboard. The process consists of four steps:

Step I: Wood chips, straw, wheat, hays, or other grains are grounded up and conveyed into moisturizing chamber. Water is either added or removed to a specific moisture content.

Step II: The mixture of woodchips and water is transferred into second chamber where MDI is added to a specific weight equivalent. Chamber is a closed system with no vent..

Step III: The combination of wood, water and MDI is mixed and then spread over a "cold plate" frame that forms a 8-inch matting. The “cold plate” moves along a conveyor system where between 5-6 frames are loaded onto a press where a hydraulic system compresses the mixture to a desired thickness between 1/4" to 5/8", The "cold plate" is heated to a design temperature. During this step the MDI reacts with the water to form a polyurethane bond with the fiber. The press is open and the trapped carbon dioxide is released. The press is equipped with a blower system that vents to the roof. The press blower is also used to exhaust the air from other parts of the process.

Step IV: The formed boards are removed from the press, checked for quality, trimmed to the designed length and width.

The controlling parameters that influence the emission rate are the temperature, flow rate and concentration of the exit gas stream. The worst-case scenario is that the exit gas stream is saturated with MDI.

The estimated MDI emission can be calculated using the following formula:

$$L = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * C_f$$

Where:

L	=	the emissions in lb/hr.
V_{air}	=	the exhaust airflow rate in ft^3/min.
T_{sp}	=	the exhaust temperature in °K.
C_{mdi}	=	the MDI concentration, in ppmv, in the exhaust air.
M_W	=	the molecular weight of MDI (250.26).
K_{MDI}	=	the adjustment factor to the vapor pressure that is a function of MDI

concentration in the feedstock and the temperature.

C_f = per cent MDI/PMDI in solution

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

C_{mdi} = $(VP_{MDI}/760) \times 10^6$

VP_{MDI} = MDI vapor pressure at exhaust temperature

14. Belts and Tire Cord

A MDI/PMDI mixture is used in belt manufacturing as a hardener. In the manufacture of belts, part of the process is to run synthetic cords through a vat solution containing a MDI/PMDI and toluene mixture and then passed it through an oven to activate the bonding process between the synthetic cord and isocyanate and dry the cord coating. The off-gases from the oven are passed through an incinerator or combustion device for destruction. Depending upon the process, the synthetic cord then goes through a number of various mixture dips and oven treatments. Once the cords have been treated, they are wound on spools for use in the belt building process.

The controlling parameters that influence the emission rate are the temperature, flow rate, concentration of the exit gas stream, reaction rate, and the unreacted fraction of MDI.. The worst-case scenario is that the exit gas stream is saturated with all the MDI that is available. The MDI emissions can be calculated using the following formula:

$$\mathbf{L = (V_{air}/359) * (273.15/T_{sp}) * 60 * (C_{mdi}/1000000) * M_W * k_{MDI} * C_f * R_{MDI}}$$

Where:

L = the emissions in lb/hr.

V_{air} = the exhaust airflow rate in ft^3/min.

T_{sp} = the exhaust temperature in °K.

C_{mdi} = the MDI concentration, in ppmv, in the exhaust air.

M_W = the molecular weight of MDI (250.26).

K_{MDI} = the adjustment factor to the vapor pressure that is a function of MDI concentration in the feedstock and the temperature.

C_f = per cent MDI/PMDI in solution

359 = the molar volume of an ideal gas in ft^3/lb-mole @ 0°C and 1-atmosphere.

C_{mdi} = $(VP_{MDI}/760) \times 10^6$

VP_{MDI} = MDI vapor pressure at exhaust temperature.

R_{MDI} = Unreacted fraction of MDI

Where:

R_{MDI} = e^(-k * t_R)

Where:

R_{MDI} = the unreacted fraction of MDI

k = the first order reaction rate constant in min^{-1}

t_R = the reaction time in minute

Appendix E – SIC Codes & NAICS Codes

Who Will Report to TRI Starting in the 1998 Reporting Year?

Metal mining (SIC code 10, except for SIC codes 1011,1081, and 1094)
Coal mining (SIC code 12, except for 1241 and extraction activities)
Electrical utilities that combust coal and/or oil (SIC codes 4911, 4931, and 4939) Resource Conservation and Recovery Act (RCRA) Subtitle C hazardous waste treatment and disposal facilities (SIC code 4953)
Chemicals and allied products wholesale distributors (SIC code 5169)
Petroleum bulk plants and terminals (SIC code 5171)
Solvent recovery services (SIC code 7389)

SIC Industry Group:

10	Metal Mining (except 1011,1081, and 1094)
12	Coal Mining (except 1241)
20	Food
21	Tobacco
22	Textiles
23	Apparel
24	Lumber and Wood
25	Furniture
26	Paper
27	Printing and Publishing
28	Chemicals
29	Petroleum and Coal
30	Rubber and Plastics
31	Leather
32	Stone, Clay, and Glass
33	Primary Metals
34	Fabricated Metals
35	Machinery (excluding electrical)
36	Electrical and Electronic Equipment
37	Transportation Equipment
38	Instruments
39	Miscellaneous Manufacturing

SIC	SIC Text	NAICS
1000	**Metal Mining**	
1021	Copper Ores	212234
1031	Lead and Zinc Ores	212231
1041	Gold Ores	212221
1044	Silver Ores	212222
1061	Ferroalloy Ores Except Vanadium	212234
1099	Miscellaneous Metal Ores, n.e.c.	212299
1200	**Coal Mining (Except 1241)**	
1221	Bituminous Coal and Lignite Surface Mining	212111
1222	Bituminous Coal Underground Mining	212112
1231	Anthracite Mining	212113

2000 Food and Kindred Products

2011	Meat packing plants.	311611
2013	Sausages and other prepared meat products.	311612
2015	Poultry slaughtering and processing.	311615
2021	Creamery products.	311512
2022	Natural, processed, and imitation cheese	311513
2023	Dry, condensed, and evaporated dairy products.	311511 or 311514
2024	Ice cream and frozen desserts.	311520
2026	Fluid milk.	311511
2035	Pickled fruits and vegetables, vegetable sauces and seasonings, and salad dressings	311421 or 311941
2037	Frozen fruits, fruit juices, and vegetables.	311411
2038	Frozen specialties, not elsewhere classified.	311212
2041	Flour and other grain mill products.	311211
2043	Cereal breakfast foods.	311230 or 311920
2044	Rice milling.	311212
2045	Prepared flour mixes and doughs.	311822
2046	Wet corn milling.	311221 or 311225
2047	Dog and cat food	311111
2048	Prepared feeds and feed ingredients for animals and fowls except dogs and cats	311119 or 311611
2051	Bread and other bakery products, except cookies and crackers.	311812
2052	Cookies and crackers .	311812, 311821, or 311919
2053	Frozen bakery products except bread.	311813
2061	Cane sugar, except refining.	311311
2062	Cane sugar refining.	311312
2063	Beet sugar	311313
2064	Candy and other confectionery products	311330 or 311340
2066	Chocolate and cocoa products.	311320 or 311330
2067	Chewing gum	311340
2068	Salted and roasted nuts	311911
2074	Cottonseed oil mills	311223 or 311225
2075	Soybean oil mills	311222
2076	Vegetable oil mills, n.e.c.	311223 or 311225
2077	Animal and marone fats and oils	311613, 311711, or 311712
2079	Shortening, table oils, margarine, and other edible fats and oils, n.e.c.	311223 or 311225
2082	Malt beverages.	311942 or 312120
2084	Wines, brandy, and brandy spirits.	312130
2085	Distilled and blended liquors	312140
2086	Bottled and canned soft drinks and carbonated waters	312111 or 312112
2087	Flavoring extracts and flavoring syrups, not elsewhere classified.	311920, 311930, 311942, or 311999
2091	Canned and cured and seafoods.	311711
2092	Prepared fresh or frozen fish or seafoods	311712
2095	Roasted coffee.	311920
2096	Potato chips, corn chips, and similar.	311919
2097	Manufactured ice.	312113
2098	Macaroni, spaghetti vermicelli, and noodles	311823
2099	Food preparations, not elsewhere classified.	111998, 311212, 311340, 311423, 311823, 311830 311911, 311920, 311941, 311942, 311991, or 311999

2100	**Tobacco products.**	
2111	Cigarettes.	312221
2121	Cigars.	312229
2131	Chewing and smoking tobacco and snuff.	312229
2141	Tobacco stemming and redrying.	312210 or 312229
2200	**Textile Mill Products**.	
2211	Broadwoven fabric mills, cotton.	313210
2221	Broadwoven fabric mills, manmade fiber, and silk	313210
2231	Broadwoven fabric mills, wool (including dyeing and finishing)	313210, 313311, or 313312
2241	Narrow fabric and other small wares mills: cotton, wool, silk, and manmade fiber.	313221
2251	Women's full-length and knee-length hosiery, except socks.	315111
2252	Hosiery, n.e.c.	313312, 315111, or 315119
2253	Knit outerwear mills.	313312, 315191, or 315192
2254	Knit underwear and nightwear mills	313312 or 315192
2257	Weft knit fabric mills	313241 or 313312
2258	Lace and warp knit fabric mills	313249 or 313312
2259	Knitting mills,n.e.c.	313241, 313249, 313249, or 315191, or 315192
2261	Finishers of broadwoven fabrics of cotton	313311
2262	Finishers of broadwoven fabrics of manmade fiber and silk.	313311
2269	Finishers of textiles, n.e.c.	313311 or 313312
2273	Carpets and rugs.	314110
2281	Yarn spinning mills.	313311
2282	Yarn texturizing, throwing, twisting, and winding mills	313211
2284	Thread mills	313113 or 313312
2295	Coated fabrics, not rubberized	313320
2296	Tire cord and fabrics	314992
2297	Nonwoven fabrics	313230
2298	Cordage and twine	313111 or 314991
2299	Textile goods, n.e.c.	313111, 313113, 313320, 313221, 313230, 313312, or 314999
2300	**Apparel and other Finished Products Made from Fabrics and Similar Materials**	
2311	Men's and boys' suits coats, and overcoats.	315211
2321	Men's and boys' shirts except work shirts.	315211 or 315223
2322	Men's and boys' underwear and nightwear.	315211 or 315221
2323	Men's and boys' neckwear.	315211 or 315993
2325	Men's and boys' separate trousers and slacks.	315211 or 315224
2326	Men's and boys' work clothing.	315211 or 315225
2329	Men's and boys' clothing, not elsewhere classified.	315211, 315228, or 315229
2331	Women's, misses', and juniors' blouses and shirts.	315212 or 315232
2335	Women's, misses', and juniors' dresses.	315212 or 315233
2337	Women's, misses', and juniors' suits, skirts, and coats.	315212 or 315234
2339	Women's, misses', and juniors' outerwear, not elsewhere classified.	315212, 315239, 315299, or 315999
2341	Women's, misses', children's, and infants' underwear and nightwear.	315231 or 315291
2342	Brassieres, girdles, and allied garments.	315212 or 315231

2353	Hats, caps, and millinery.	315211, 315212, or 315991
2361	Girls', children's, and infants' dresses, blouses, and shirts.	315211, 315212, 315223, 315232, 315233, or 315291
2369	Girls', children's, and infants' outerwear, NEC	315211, 315212, 315221, 315222, 315224, 315228, 315231, 315234, 315239, or 315291
2385	Waterproof outerwear.	315211, 315222, 315228, 315234, 315239, 315291, or 315999
2386	Leather and sheep lined clothing	315211, 315212, or 315292.
2387	Apparel belts.	315211, 315212, or 315999
2389	Apparel and accessories, not elsewhere classified.	315211, 315212, 315231, 315299, or 315999
2391	Curtains and draperies.	314121
2392	House furnishings, except curtains and draperies.	314129, 314911, 314999, or 339994,
2393	Textile bags.	314911
2394	Canvas and related products	314912
2395	Pleating, decorative and novelty stitching, and tucking for the trade.	314999, 315211, or 315212
2396	Automotive trimmings, apparel findings, and related products.	314999, 315211, 315212, 315999, 323113, or 336360
2397	Schiffi machine embroideries	313222
2399	Fabricated textile products, not elsewhere classified.	315211, 315212, 315999, or 336360

2400 Lumber and Wood Products, Except Furniture

2411	Logging	113310
2421	Sawmills and planing mills, general.	321113, 321912, 321918, 321920, or 321999
2426	Hardwood dimension and flooring	321113, 321912, 321918, or 337215
2429	Special product sawmills, n.e.c.	321113, 321920, 321999, 321911, or 321918
2431	Millwork.	321918
2434	Wood kitchen cabinets.	337110
2435	Hardwood veneer and plywood.	321211
2436	Software veneer and plywood	321212
2439	Structural wood members	321213 or 321214
2441	Nailed and lock corner wood boxes and shook	321920
2448	Wood pallets and skids.	321920
2449	Wood containers	321920
2451	Mobile homes.	321991
2452	Prefabricated wood buildings and components	321992
2491	Wood preserving.	321114
2493	Reconstituted wood products	321219
2499	Wood products, not elsewhere classified.	321920, 321999, 333415, 337125, 339113, or 339999

2500 Furniture and fixtures

2511	Wood household furniture, except upholstered.	337122 or 337215
2512	Wood household furniture, upholstered.	337121
2514	Metal household furniture.	337121, 337124, or 337215
2515	Mattresses foundations, and convertible beds.	337121, or 337910
2517	Wood television, radio, phonograph, and sewing machine cabinets.	337129
2519	Household furniture, not elsewhere classified.	337125
2521	Wood office furniture.	337211
2522	Office furniture except wood.	337214
2531	Public building and related furniture.	336360, 337127, or 339942
2541	Wood office and store fixtures, partitions, shelving,	337110, 337127, 337212, or 337215

	and lockers.	
2542	Office and store fixtures, partitions, shelving, and lockers, except wood.	337127 or 337215
2591	Drapery hardware and window blinds and shades.	337920
2599	Furniture and fixtures, not elsewhere classified.	337127 or 339111
2600	**Paper and Allied Products.**	
2611	Pulp mills.	322110
2621	Paper mills.	322121 or 322122
2631	Paperboard mills.	322130
2652	Setup paperboard boxes.	322213
2653	Corrugated and solid fiber boxes.	322211
2655	Fiber cans, tubes drums, and similar products.	322214
2656	Sanitary food containers, except folding	322215
2657	Folding paperboard boxes, including sanitary.	322212
2671	Packaging paper and plastics film, coated and laminated.	322221 or 326112
2672	Coated and laminated paper, not elsewhere classified.	322222
2673	Plastics, foil, and coated paper bags.	322223
2674	Uncoated paper and multi-wall bags.	322224
2676	Sanitary paper products.	322291
2677	Envelopes.	322232
2678	Stationery, tablets, and related products. `	322233
2679	Converted paper and paperboard products, not elsewhere classified.	322211, 322222, 322231 or 322299
2700	**Printing, Publishing, and Allied Industries.**	
2711	Newspapers: publishing, or publishing and printing.	511110, 516110, 511120 or 516110
2731	Books: publishing, or publishing and printing.	511130, 512230 or 516110
2732	Book printing.	323117
2741	Miscellaneous publishing.	511120, 511130, 511140, 511199, 512230 or 516110
2752	Commercial printing, lithographic.	323110 or 323114
2754	Commercial printing, gravure.	323111
2759	Commercial printing, not elsewhere classified.	323112, 323113, 323114, 232115 or 323119
2761	Manifold business forms.	323116
2771	Greeting cards	323110-323113, 232119, 511191 or 516110
2782	Blank books, loose-leaf binders and devices.	323116 or 323118
2789	Bookbinding and related work	323121
2291	Typesetting	323122
2796	Plate making and related services.	323122
2800	**Chemicals and Allied Products.**	
2812	Alkalies and chlorine	325181
2813	Industrial gases.	325120
2816	Inorganic gases	325131 or 325182
2819	Industrial inorganic chemicals, not elsewhere classified.	211112, 325131, 325188, 325998 or 331311
2821	Plastics materials, synthetic resins, and non-vulcanizable elastomers.	325211
2822	Synthetic rubber (vulcanizable elastomers).	325212
2823	Cellulosic manmade fibers	325221
2824	Manmade organic fibers, except cellulosic	325222

2833	Medicinal chemicals and botanical products.	325411
2834	Pharmaceutical preparations.	325412
2835	In vitro and in vivo diagnostic substances.	325412 or 325413
2836	Biological products, except diagnostic substances.	325414
2841	Soap and other detergents, except specialty cleaners.	325611
2842	Specialty cleaning, polishing, and sanitation preparations.	325612
2843	Surface active agents, finishing agents, sulfonated oils, and assistants	325613
2844	Perfumes, cosmetics, and other toilet preparations.	325611
2851	Paints, varnishes, lacquers, enamels, and allied products.	325510
2860	Industrial organic chemicals.	
2861	Gum and wood chemicals	325191
2865	Cyclic organic crudes and intermediates, and organic dyes and pigments.	325110, 325132 or 325192
2869	Industrial organic chemicals, not elsewhere classified.	325110, 325120, 325188, 325192, 325193, 325199 or 325998
2873	Nitrogenous fertilizers.	325311
2874	Phosphatic fertilizers	325312
2875	Fertilizers, mixing only	325314
2879	Pesticides and agricultural chemicals, NEC 325320	
2891	Adhesives and sealants.	325520
2892	Explosives	325920
2893	Printing ink	325910
2895	Carbon black	325182
2899	Chemicals and chemical preparations, NEC	311942, 325199, 325510 or 325998
2900	**Petroleum Refining and Related Industries.**	
2911	Petroleum refining.	324110
2951	Asphalt paving mixtures and blocks.	324121
2952	Asphalt felts and coatings.	324122
2992	Lubricating oils and greases.	324191
2999	Products of petroleum and coal, n.e.c.	324199
3000	**Rubber and Miscellaneous Plastics Products.**	
3011	Tires and inner tubes	326211
3021	Rubber and plastic footwear	316211
3052	Rubber and plastics hose and belting	326220
3053	Gaskets, packing, and sealing devices.	339991
3061	Molded, extruded and lathe cut mechanical rubber products	326291
3069	Fabricated rubber products, NEC	313320, 314911, 315299, 315999, 326192, 326299, 339113, 339920 or 339932
3081	Unsupported plastics film and sheet.	326113
3082	Unsupported plastics profile shapes.	326121
3083	Laminated plastics plate, sheet, and profile shapes.	326130
3084	Plastics pipe.	326122
3085	Plastics bottles.	326160
3086	Plastics foam products.	326140 or 326150
3087	Custom compounding of purchased plastics resin.	325991
3088	Plastics plumbing fixtures.	326191
3089	Plastics products, not elsewhere classified.	326121, 326122, 326199, 337215 or 339113

3100 Leather and Leather Products.

3111	Leather tanning and finishing	316110
3131	Boot and shoe cut stock and findings.	316999, 321999 or 339993
3142	House slippers.	316212
3143	Men's footwear, except athletic.	316213
3144	Women's footwear, except athletic.	316214
3149	Footwear, except rubber, not elsewhere classified.	316219
3151	Leather gloves and mittens.	315211, 315212 or 315992
3161	Luggage.	316991
3171	Women's handbags and purses.	316992
3172	Personal leather goods, except women's handbags and purses.	316993 or 339914
3199	Leather goods, n.e.c.	316999

3200 Stone, Clay, Glass, and Concrete Products.

3211	Flat glass.	327211
3221	Glass containers	327213
3229	Pressed and blown glass and glassware, n.e.c.	327212
3231	Glass products, made of purchased glass.	327215
3241	Cement, hydraulic.	327310
3251	Brick and structural clay tile	327121 or 327331
3253	Ceramic wall and floor tile	327122
3255	Clay refractories	327124
3261	Vitreous china plumbing fixtures and china and earthenware fittings and bathroom accessories.	327111
3262	Vitreous china table and kitchen articles	327112
3263	Fine earthenware (white ware) table and kitchen articles	327112
3264	Porcelain electrical supplies	327113
3269	Pottery products, not elsewhere classified.	327112
3271	Concrete block and brick.	327331
3272	Concrete products, except block and brick.	327332, 327390 or 327999
3273	Ready-mixed concrete.	327320
3274	Lime.	327410
3275	Gypsum products.	327420
3281	Cut stone and stone products.	327991
3291	Abrasive products	327910 or 332999
3292	Asbestos products	327999, 336340 or 336350
3295	Minerals and earths, ground or otherwise treated.	212324, 212325, 212393, 212399 or 327992
3296	Mineral wool.	327993
3297	Non-clay refractories	327125
3299	Nonmetallic mineral products, n.e.c.	327112, 327420 or 327999

3300 Primary Metal Industries.

3312	Steel works, blast furnaces (including coke ovens), and rolling mills.	324199, 331111 or 331221
3313	Electrometallurgical products, except steel	331112
3315	Steel wiredrawing and steel nails and spikes	331222
3317	Steel pipe and tubes.	331210
3321	Gray and ductile iron foundries	331511
3322	Malleable iron foundries	331511

3324	Steel investment foundries	331512
3325	Steel foundries, n.e.c.	331513
3331	Primary smelting and refining of copper	331411
3334	Primary production of aluminum	331312
3339	Primary smelting and refining of nonferrous, except copper and aluminum	331419
3341	Secondary smelting and refining of nonferrous metals.	331314, 331423 or 331492
3351	Rolling, drawing, and extruding of nonferrous metals.	331421
3353	Aluminum sheet, plate, and foil.	331315
3354	Aluminum extruded products.	331316
3355	Aluminum rolling and drawing, n.e.c.	331319
3356	Rolling, drawing, and extruding of nonferrous metal, except copper and aluminum	331491
3357	Drawing and insulating of nonferrous wire	331319, 331422, 331491, 335921 or 335929
3363	Aluminum die-casting	331521
3364	Nonferrous die-casting, except aluminum	331522
3365	Aluminum foundries.	331524
3366	Copper foundries	331525
3369	Nonferrous foundries, except aluminum and copper.	331528
3398	Metal heat-treating.	332811
3399	Primary metal products, not elsewhere classified.	331111, 331221, 331314, 331423, 331492, 332618 or 332813

3400 Fabricated Metal Products, Except Machinery and Transportation Equipment.

3411	Metal cans.	332431
3412	Metal shipping barrels, drums, kegs, and pails.	332439
3421	Cutlery.	332211 or 332212
3423	Hand and edge tools, except machine tools and handsaws.	332212
3425	Handsaw and saw blades	332213
3429	Hardware, not elsewhere classified.	332439, 332510, 332722, 332919, 332999, 333923, 334518, 336399 or 337215
3431	Enameled iron and metal sanitary ware	332998
3432	Plumbing fixture fittings and trim	332913, 332919 or332999
3433	Heating equipment, except electric and warm air furnaces.	333414
3441	Fabricated structural metal.	332312
3442	Metal doors, sash, frames, molding, and trim.	332321
3443	Fabricated plate work (boiler shops).	332313, 332410, 332420 or 333415
3444	Sheet metal work.	332321, 332322, 332439 or 333415
3446	Architectural and ornamental metal work.	332323
3448	Prefabricated metal buildings and components	332311
3449	Miscellaneous structural metal work.	332114, 332312 or 332323
3451	Screw machine products	332721
3452	Bolts, nuts, screws, rivets, and washers.	332722
3462	Iron and iron forgings	332111
3463	Nonferrous forgings	332112
3465	Automotive stampings	336370
3466	Crown and closures	332115
3469	Metal stampings, not elsewhere classified.	332116, 332214 or 332439
3471	Electroplating, plating, polish anodizing and coloring.	332813
3479	Coating, engraving and allied services, n.e.c.	332812, 339911, 339912 or 339914
3482	Small arms ammunition	332992

3483	Ammunition, except for small arms	332993
3484	Small arms	332994
3489	Ordnance and accessories, n.e.c.	332995
3491	Industrial valves	332911
3492	Fluid power valves and hose fittings	332912
3493	Steel springs, except wire	332611
3494	Valves and pipe, fittings, not else where classified.	332919 or 332999
3495	Wire springs.	332612 or 334518
3496	Miscellaneous fabricated wire products.	332214, 332618 or 333924
3497	Metal foil and leaf	322225 or 332999
3498	Fabricated pipe and pipe fittings.	332996
3499	Fabricated metal products, not elsewhere classified.	332117, 332439, 332510, 332919, 332999, 336360 or 337215

3500 Industrial and Commercial Machinery and Computer Equipment.

3511	Steam, gas and hydraulic turbines, and turbine generator set units	333611
3519	Internal combustion engines, n.e.c.	333618 or 336399
3523	Farm machinery and equipment	332212, 332323, 333111 or 333922
3524	Lawn and garden tractors and home lawn and garden equipment	332212 or 333112
3531	Construction machinery and equipment.	333120, 333923 or 336510
3532	Mining machinery and equipment, except oil and gas field machinery and equipment.	333131
3534	Elevators and moving stairways.	333921
3535	Conveyors and conveying equipment.	333922
3536	Overhead traveling cranes, hoists, and monorail systems	333923
3537	Industrial trucks, tractors, trailers, and stackers	332439, 332999 or 333924
3541	Machine tools, metal-cutting types.	333512
3542	Machine tools, metal-forming types	333513
3543	Industrial pattern	332997
3544	Special dies and tools, die sets, jigs and fixtures, and industrial molds.	333511 or 333514
3545	Cutting tools, machine tool accessories, and machinists' precision measuring devices.	332212 or 333515
3546	Power driven hand tools.	333991
3547	Rolling mill machinery and equipment.	333516
3548	Electric and gas welding and soldering equipment	333992 or 335311
3549	Metal working machinery, n.e.c.	333518
3552	Textile machinery	333292
3553	Woodworking machinery	333210
3554	Paper industry machinery	333291
3555	Printing trades machinery and equipment.	333293
3556	Food products machinery	333294
3559	Special industrial machinery, n.e.c.	332410, 333111, 333220, 333295, 333298 or 333319
3561	Pumps and pumping equipment	333911
3562	Ball and roller bearings.	332991
3563	Air and gas compressors.	333912
3564	Industrial and commercial fans and blowers and air purification equipment.	333411 or 333412
3565	Packaging equipment	333993
3566	Speed changers, industrial high speed drives, and gears	333612

3567	Industrial process furnaces and ovens	333994
3568	Mechanical power transmission equipment, NEC	333613
3569	General industrial machinery and equipment, NEC	314999, 333414 or 333999
3571	Electronic computers.	334111
3572	Computer storage devices.	334112
3575	Computer terminals	334113
3577	Computer peripheral equipment, not elsewhere classified.	334119, 334418 or 334613
3578	Calculating and accounting machines, except computers	333311, 333313 or 334119
3579	Office machines, not elsewhere classified.	333313, 334518 or 339942
3581	Automatic vending machines	333311
3582	Commercial laundry, dry cleaning, and pressing machines	333312
3585	Air-conditioning and warm air heating equipment and commercial and industrial refrigeration equipment.	333415 or 336391
3586	Measuring and dispensing pumps	333913
3589	Service industry machinery, not elsewhere classified.	333319
3592	Carburetors, pistons, piston rings, and valves.	336311
3593	Fluid power cylinders and actuators	333995
3594	Fluid power pumps and motors	333996
3596	Scales and balances, except laboratory.	333997
3599	Industrial and commercial machinery and equipment, NEC	332710, 332813, 332999, 333319, 333999, 334519 or 336399

3600 Electronic and other Electrical Equipment and Components, Except Computer Equipment.

3612	Power, distribution, and specialty transformers.	335311
3613	Switchgear and switchboard apparatus.	335313
3621	Motors and generators.	335312
3624	Carbon and graphite products.	335991
3625	Relays and industrial controls.	335314
3629	Electrical industrial apparatus, not elsewhere classified.	335999
3631	Household cooking equipment	335221
3632	Household refrigerators and home and farm freezers	335222
3633	Household laundry equipment	335224
3634	Electrical house wares and fans	333414, 335211 or 339999
3635	Household vacuum cleaners	335212
3639	Household appliances, not elsewhere classified.	333298, 335212 or 335228
3641	Electric lamp bulbs and tubes.	335110
3643	Current-carrying wiring devices.	335931
3644	Non-current-carrying wiring devices.	332212 or 335932
3645	Residential electric lighting fixtures.	335121
3646	Commercial, industrial, and institutional electric lighting fixtures.	335122
3647	Vehicular lighting equipment	336321
3648	Lighting equipment, not elsewhere classified.	335129
3651	Household audio and video equipment.	334310
3652	Phonograph records and pre-recorded audiotapes and disks.	334612 or 512220
3661	Telephone and telegraph apparatus.	334210 or 334418
3663	Radio and television broadcasting and communications equipment.	334220
3669	Communications equipment, not elsewhere classified.	334290
3671	Electron tubes	334411
3672	Printed circuit boards.	334412

3674	Semiconductors and related devices.	334413
3675	Electronic capacitors	334414
3676	Electronic Capacitors	334414
3677	Electronic coils, transformers and other inductors.	334416
3678	Electronic connectors.	334417
3679	Electronic components, not elsewhere classified.	334220, 334310, 334418 or 334419
3691	Storage batteries	335911
3692	Primary batteries dry and wet.	335912
3694	Electrical equipment for internal combustion engines.	336322
3695	Magnetic and optical recording media	334613
3699	Electrical machinery, equipment, and supplies, n.e.c.	333319, 333618, 333992, 335129 or 335999

3700 Transportation Equipment.

3711	Motor vehicles and motor vehicle equipment.	336111, 336112, 336120, 336211 or 336992
3713	Truck and bus bodies.	336211
3714	Motor vehicle parts and accessories.	336211, 336312, 336322, 336330, 336340, 336350 or 336399
3715	Truck trailers	336212
3716	Motor homes	336213
3721	Aircraft.	336411 or 541710
3724	Aircraft engines and parts	336412 or 541710
3728	Aircraft parts and auxiliary equipment, NEC	332912, 336411, 336413 or 541710
3731	Ship building and repairing.	336611 or 488390
3732	Boat building and repairing.	336612 or 811490
3743	Railroad equipment	333911 or 336510
3751	Motorcycles, bicycles and parts	336991
3761	Guided missiles and space vehicle	336414 or 541710
3764	Guided missile and space vehicle propulsion units and propulsion parts	336415 or 541710
3769	Guided missile and space vehicle parts and auxiliary equipment, n.e.c.	336419 or 541710
3792	Travel trailers and campers.	336214
3795	Tanks and tank components	336992
3799	Transportation Equipment, n.e.c.	

3800 Measuring, Analyzing, and Controlling Instruments; Photographic, Medical, and Optical Goods, Watches and Clocks.

3812	Search, detection, navigation, guidance, aeronautical, and nautical systems instruments, and equipment.	334511
3821	Laboratory apparatus and furniture.	339111
3822	Automatic controls for regulating residential and commercial environments and appliances.	334512
3823	Industrial instruments for measurement, display, and control of process variables; and related products.	334513
3824	Totalizing fluid meters and counting devices.	334514
3825	Instruments for measuring and testing of electricity and electrical signals.	334514 or 334515
3826	Laboratory analytical instruments	334516
3827	Optical instruments and lenses	333314
3829	Measuring and controlling devices not elsewhere classified.	334514, 334518, 334519 or 339112
3841	Surgical and medical instruments and apparatus.	332994, 339111 or 339112

3842	Orthopedic, prosthetic, and surgical appliances and supplies.	322291, 334510, 339113 or 339999
3843	Dental equipment and supplies.	339114
3844	X-ray apparatus and tubes and related irradiation apparatus.	334517
3845	Electro medical and electrotherapeutic apparatus.	334510 or 334517
3851	Ophthalmic goods.	339113 or 339115
3861	Photographic equipment and supplies.	325992 or 333315
3873	Watches, clocks, clockwork operated devices, and parts.	334518
3900	**Miscellaneous Manufacturing Industries.**	
3911	Jewelry, precious metal.	339911
3914	Silverware, plated ware, and stainless steel ware.	332211, 332999 or 339912
3915	Jewelers' findings and materials, and lapidary work.	334518 or 339913
3931	Musical instruments.	339992
3942	Dolls and stuffed toys.	339931
3944	Games, toys and children's vehicles; except dolls and bicycles	3366991 or 339932
3949	Sporting and athletic goods, not elsewhere classified.	339920
3951	Pens, mechanical pencils, and parts.	339941
3952	Lead pencils, crayons, and artists' materials.	325998, 337127 or 339942
3953	Marking devices.	339943
3955	Carbon paper and ink ribbons	339944
3961	Costume jewelry and costume novelties, except precious metal.	339914 or 339993
3965	Fasteners, buttons, needles, and pins.	339993
3991	Brooms and brushes.	339994
3993	Signs and advertising specialties.	323113 or 339950
3995	Burial caskets.	339995
3999	Manufacturing industries not elsewhere classified.	316110, 321999, 325998, 326199, 332211, 332212, 332812, 332999, 333319, 335121, 335211, 337127 or 339999
4900	**Electric, Gas, and Sanitary Services (limited to 4911, 4931, 4939, and 4953)**	
4911	Electric Services (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce)	221111, 221112, 221113, 221119, 221121 or 221122
4931	Electric and Other Services Combined (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce)	221111, 221112, 221113, 221119, 221121, 221122 or 221210
4939	Combination utilities, n.e.c. (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce)	221111, 221112, 221113, 221119, 221121, 221122 or 221210
4953	Refuse Systems (limited to facilities regulated under the RCRA Subtitle C, 42 U.S.C. section 6921 *et seq.*)	562211, 652212, 562213, 562219 or 562920
5100	**Wholesale Trade-Nondurable Goods(Limited to 5169 and 5171)**	
5169	Chemical and allied Products, n.e.c.	424690, 425110 or 425120
5171	Petroleum Terminals and bulk stations	424710, 454311 or 454312
7300	Business Services (limited to 7389)	
7389	Business services, n.e.c. (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis.	

Appendix F: For Future Reference

Appendix G – Glossary

AP-42	the EPA document, Compilation of Air Pollutant Emission Factors, which contains information on over 200 stationary source categories. This information includes brief descriptions of processes used, potential sources of air emissions from the processes, and in many cases, common methods used to control these air emissions.
Covered Facility	a facility defined in 40 CFR Section 372.3 that has 10 or more full-time employees, is in a covered SIC code and meets the activity threshold for manufacturing, processing, or otherwise using a listed toxic chemical (40 CFR Section 372.22).
Covered SIC Code	prior to 1/1/1998 SIC code 20 through 39. Beginning 1/1/1998 SIC Code 10 (except 1011,1081,and 1094), 12 (except1241), or 20-39; industry codes4911, 4931, or 4939 (limited to facilities that combust coal and/or oil for the purpose of generating power for distribution in commerce): or 4953 (limited to facilities regulated under the RCRA, subtitle C,42U.S.C. Section 6921 et seq.) or 5169, or 5171, or 7389 (limited to facilities primarily engaged in solvent recovery (40 CFR Section 372.22(b).
Disposal	any underground injection, placement in landfills/surface impoundments, land treatment, or other intentional land disposal (40 CFR Section 372.3).
Environment	includes water, air, and land and the interrelationship that exists among and between water, air, and land and all living things (EPCRA Section 329(2)).
Facility	all buildings, equipment, structures and other stationary items which are located on a single site or contiguous or adjacent sites and which are owned or operated by the same person (or by any person which controls, is controlled by or under common control with such person) (40 CFR Section 372.3).
Full-time Employee	a person who works 2,000 hours per year of full time equivalent employment. A facility would calculate the number of full-time employees by totaling the hours worked during the calendar year by all employees, including contract employees, and dividing the total by 2,000 hours (40 CFR Section 372.3)
Manufacture	to produce, prepare, import, or compound a toxic chemical. Manufacture also applies to a toxic chemical that is produced coincidentally during the manufacture, processing, use, or disposal of another chemical or mixture of chemicals, including a toxic chemical that is separated from that other chemical or mixture of chemicals as a byproduct, and a toxic chemical that remains in that other chemical or mixture of chemicals as an impurity (40 CFR Section 372.3).
Mixture	any combination of two or more chemicals if the combination is not, in whole or in part, the result of a chemical reaction. However, if the combination was produced by a chemical reaction, but could have been produced without a chemical reaction, it is also treated as a mixture. A mixture also includes any combination that consists of a chemical and associated impurities (40CFR Section 372.3). A waste is not considered a mixture for EPCRA Section 313 reporting purposes.
Otherwise Use	any use of a toxic chemical that is not covered by the terms manufacture or process, and includes use of a toxic chemical contained in a mixtures or trade name product. Relabeling or redistributing a container of a toxic chemical where no repackaging of the

	toxic chemical occurs does not constitute use or processing of the toxic chemical Otherwise use of a toxic chemical does not include disposal, stabilization (without subsequent distribution in commerce), or treatment for destruction unless the toxic chemical that was disposed, stabilized or treated for destruction was received from off-site for the purposes of further waste management or it was disposed, stabilized, or treated for destruction as a result of waste management activities on materials received from off-site for the purposes of further waste management activities.
Release	any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of barrels, containers, and other closed receptacles) of any toxic chemicals (40 CFR Section 372.2).
Total Annual Reportable Amount	a facility's total reportable amount is equal to the combined total quantities released at the facility (including disposal), treated at the facility (as represented by amounts destroyed or converted by treatment processes), recovered at the facility as a result of recycle operations, combusted for the purpose of energy recovery at the facility, and the amounts transferred from the facility to off-site locations for the purpose of recycling, energy recovery, treatment, and/or disposal.
Toxic Chemical	a chemical or chemical category listed in 40 CFR Section 372.65 (40 CFR Section 372.3).

Appendix H - Request For Withdrawal

Facility Name
Facility Mailing Address

Date:

TRI Data Processing Center
P.O. Box 1513
Lanham, MD 20703-1513
Attention: TRI Withdrawal Request

To whom it may concern:

(Fill in your facility name and TRIFID here) is requesting a withdrawal for the following submissions filed under EPCRA Section 313 from EPA's database (i.e. the Toxic Release Inventory System (TRIS)):

Chemical Name Reported:
CAS Number/Category Code:
Report Type (please check one): **Form R * * Form A Certification * *
Reporting Year:
Reason (s) for Withdrawal:

The technical contact is: (Insert name here) and may be reached at: (Insert telephone number here.

Requester's Name:
Requester's Signature:
Address: (If different from facility address or facility mailing address)

Make certain that a copy of Form R or Form A Certification that you want to withdraw is sent along with the request for withdrawal and also submit a copy of the request to the appropriate state agency, if required.

Appendix H - Request For Revision

Facility Name
Facility Mailing Address

Date:

TRI Data Processing Center
P.O. Box 1513
Lanham, MD 20703-1513
Attention: TRI Revision Request

To whom it may concern:

(Fill in your facility name and TRIFID here) is requesting a revision for the following submissions filed under EPCRA Section 313 from EPA's database (i.e. the Toxic Release Inventory System (TRIS)):

Chemical Name Reported: _____
CAS Number/Category Code: _____
Report Type (please check one): **Form R * * Form A Certification * ***
Reporting Year: _____
Reason (s) for Withdrawal: _____
_____
_____
_____

The technical contact is: (Insert name here) and may be reached at: (Insert telephone number here. _____

Requester's Name: _____
Requester's Signature: _____
Address: (If different from facility address or facility mailing address)
_____
_____

Please include a copy of Form R or Form A Certification (revision box checked) you want to revise.

Please submit a copy of the request to the appropriate state agency, if required.

Appendix I – References

1. U.S. EPA, December 1987, *Estimating Releases and Waste Treatment Efficiencies for the Toxic Release Inventory Form,* EPA Office of Pollution Prevention and Toxics, EPA Publication No. 560/4-88-002.

2. Power, R.W., 1984, *"Estimating Worker Exposure to Gases and Vapors Leaking from Pumps and Valves,"* American Industrial Hygiene Association Journal, 45, A7-A-15.

3. Chakrabarti, A., *Vapor Pressure of Diphenylmethane Diisocyanate (MDI) Formulations,* The Dow Chemical Company, Midland, Michigan.

4. *Compilation of Air Pollutant Emission Factors*, AP-42, Fifth Edition, Volume I: Stationary Point and Area Sources, Chapter 7 Liquid Storage Tanks.

5. *Form R: Reporting of Binder Chemicals Used in Foundries*, 2nd Edition, 1998, American Foundrymen's Society, Inc. and Casting Industry Suppliers Association

6. *U.*S. EPA Toxic Chemical Release Inventory Reporting Forms and Instructions, Revised 2002 Version, Section 313 of the Emergency Planning and Community Right-to Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986).

7. MDI Emissions Estimator, Version 3.0,February 2004, Alliance for the Polyurethane Industry

Reference Number: AX186

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INDUSTRY

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